1

Turbidity

Introduction

Turbidity in water is caused by suspended matter such as clay, slit, finely divided organic and inorganic matter solubles, coloured organic compounds and plankton and other microscopic organisms. Turbidity is an expression of optical properly that uses light scattering properties of suspension in the sample. Optically black particles such as those of activated carbon may absorb light and effectively increases turbidity measurements. By using a turbidity meter we can easily determine the tubidity of the liquid specially water.

What Causes Turbidity?

Turbidity is a natural phenomenon that occurs in most bodies of water, be it oceans, lakes or rivers. A major source of Turbidity in the open waters of many lakes and rivers is typically phytoplankton. Closer to the lakeshore, particulates may also include clays and silts from shoreline erosion, resuspended bed sediments and organic detritus from streams. Bottom-feeding fish like carp can stir up sediments on the bed and increase the cloudiness of the water as can the excessive growth of algae. Turbidity also occurs in oceans. Like lakes, highly turbid ocean waters have a large number of particulates in them where the visibility into the water is reduced by scattering particles like sediments and phytoplankton. Turbidity can also have anthropogenic origins These may vary from wastewater discharges to beam trawling, propeller wash resulting from shipping and re-suspension caused by dredging.

Is Turbidity Unusual or Unnatural?

Turbidity is a background quality in all bodies of water. Increased Turbidity can be caused by natural events such as storms, heavy rains and floods, which create fast running water that can carry more particles and larger-sized sediment. This increased flow can pick up sand, silt, clay, and organic particles from the land and carry it to surface water thus affecting Turbidity. For instance, after a hurricane makes landfall, an increase in Turbidity can be seen as a result of sediments that have been resuspended from the shallow bottom regions. In near-shore areas, some Turbidity may also come from sediments eroded from beaches as well as from sediment-laden river plumes.Suspended matter such as clay, silt, and organic matter, as well as plankton and other microscopic organisms, which interfere with the passage of light through the water, can cause Turbidity. These may be known as the total suspended solids (TSS). The greater the amount of TSS in the water, the murkier it appears, and the higher the measured Turbidity.

Why is Turbidity Important?

Increased Turbidity can disrupt the natural environment and hinder the growth of flora and fauna. When sunlight is blocked from penetrating through the water, for instance, high concentrations of particulate matter may modify light penetration, causing shallow lakes and bays to fill in faster and smother benthic habitats. This impacts both underwater organisms and their eggs. If light penetration is reduced significantly, it may reduce photosynthesis which in turn may lower the daytime release of oxygen into the water. Reduced light penetration also has a sensory impact by preventing various organisms from seeing their food, their preys and predators, their mates and offspring. This is true whether increased Turbidity is caused by natural or unnatural events. On the other hand, some species of flora and fauna are used to natural variability in Turbidity and can well survive periods with less sunlight up to a certain level

Units of Turbidity

- Because optical properties depend on suspended particle size, a stable synthetic material called "Formazin" with uniform particle size is often used as a standard for calibration and reproducibility. The unit is called Formazin Turbidity Unit (FTU).
- Nephelometric Turbidity Units (NTU) specified by United States Environmental Protection Agency is a special case of FTU, where a white light source and certain geometrical properties of the measurement apparatus are specified. (Sometimes the alternate form "nephelos turbidity units" is used
- Formazin Nephelometric Units (FNU), prescribed for 9 measurements of turbidity in water treatment by ISO 7027, another special case of FTU with near infrared light (NIR) and 90° scatter.
- Formazin Attenuation Units (FAU) specified by ISO 7027 for water treatment standards for turbidity measurements at 0°, also a special case of FTU.
- Formazin Backscatter Units (FBU), not part of a standard, is the unit of optical backscatter detectors (OBS), measured at c. 180°, also a special case of FTU.
- European Brewery Convention (EBC) turbidity units
- Concentration Units (C.U.)
- Optical Density (O.D.)
- Jackson "Candle" Turbidity Units (JTU; an early measure)
- Helms Units
- American Society of Brewing Chemists (ASBC-FTU) turbidity units
- Parts Per Million of standard substance, such as PPM/DE (Kieselguhr)
- "Trübungseinheit/Formazin" (TE/F) a German standard, now replaced by the FNU unit.
- Diatomaceous earth ("ppm SiO_2") an older standard, now obsolete

A more popular term for this instrument in water quality testing is a *turbidimeter*. However, there can be differences between models of turbidimeters, depending upon the arrangement (geometry) of the source beam and the detector. A nephelometric turbidimeter always monitors light reflected off the particles and not attenuation due to cloudiness. In the United States environmental monitoring the turbidity

standard unit is called Nephelometric Turbidity Units (NTU), while the international standard unit is called Formazin Nephelometric Unit (FNU). The most generally applicable unit is Formazin Turbidity Unit (FTU), although different measurement methods can give quite different values as reported in FTU (see below).

Gas-phase nephelometers are also used to study the atmosphere. These can provide information on visibility and atmospheric albedo. Gas-phase nephelometers are also used in the detection ofsmoke & other particles of combustion. In such use, the apparatus is referred to as an aspirated smoke detector. These have the capability to detect extremely low particle concentrations (to 0.005%) and are therefore highly suitable to protecting sensitive or valuable electronic equipment, such as mainframe computers and telephone switches.

The Digital Turbidity Meter is a very accurate and stable instrument for measurement of turbidity up to 1000 NTU.

1.	**Technical Specifications**	
	Range	0 to 1000NTU
	Accuracy	I: 3% of full scale in 0-1 000 NTU.
	Test Tube System	30 mm clear glass test tube.
	Light Source	6V, 300mA, tungsten lamp
	Display	31/2 digit bright red LED display
	Detector	Photocell/Photodiode
	Calibration	With formazine solution
	Power Supply	230V:I: 10% ACt 50 Hz with built-in voltage stabilizer.
	Dimensions	275Lx 175Wx 115H mm
2.	**Standard Accessories**	
	Test Tubes (Matched)	1 Set.
	Instruction Manual	1 No.
	Dust Cover	1 No.
	Main Lead	1 No.

USER CONTROLS AND DISPLAY (see fig 1 and 2)

Display : 3½ digit, bright Red LED display for accurate reading of turbidity.

Test Tube Holder: The test tube holder keeps the test tube containing solutions to be tested.

Range Switch: It is a two position selector switch with 200 & 1000 NTU range. The resolution of the instrument is 1 NTU

Set Zero: This control is used to set Zero of the display, when test tube containing distilled water is inserted in the tube holder & Lid is closed.

Calibrate: This control is a 10 turn pot for calibration of the instrument with standard solution in the light path.

ON/OFF Switch: This is a two position toggle Switch used to switch ON the power to the instrument. The instrument must be switched OFF when not in use.

Test Tube Holder Lid: The Lid of the test tube holder prevents external light to enter the solution under test.

Operating Instructions

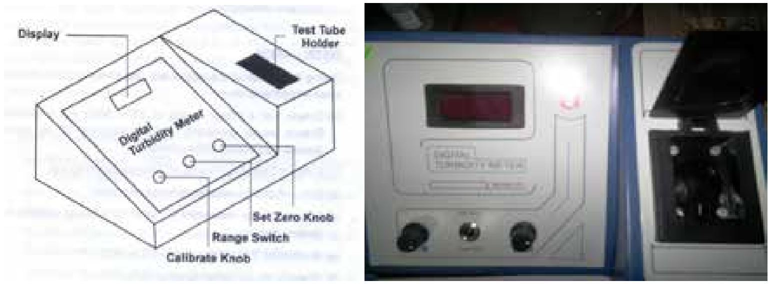


Fig. 1 & 2: Showing the Diagram and Picture of the Digital Turbidity meter model 331 Electronics India

Instructions

(a) Take out your Digital Turbidity Meter and accessories from the card board box.

(b) Check all the accessories as per list given in the instruction manual of the instrument provided with the instrument.

Installation

During installation of the instrument, the following points must be taken into consideration:

(a) Ensure that a Power Supply of 230V, 5OHz AC is available and also ensure proper grounding of the instrument for its smooth operation and safety of the operator.

(b) Connect 3 pin plug in S amp. AC Voltage supply socket.
(c) Ensure thatthe environment is free from dust.
(d) Ensure that the instrument is placed on a strong vibration free working bench.
(e) Room temp.
(f) Humidity should not be more than 90%.
(g) Switch on the instrument.
(h) Insert a test tube containing distilled water in the test tube holder.
(i) Set 000 on the instrument display by rotating the “SET ZERO”Knob.
(j) Now the instrument is ready for use.

Calibration

The calibration of the instrument is done by the use of standard solutions, in this case turbidity free water is needed. Turbidity free water is difficult to obtain. The following method is satisfactory for obtaining turbidity as low as 0.02 NTU. Pass distilled water through a membrane filter having precision-sized holes of 0.2mm, the usual membrane filter used for bacteriological examinations is not satisfactory. Rinse collecting flask at least twice with filtered water discard the next 200 ml. filtered water. Some commercial bottled demineralized waters are nearly particle-free. These may be used when their turbidity is lower than that can be achieved in the laboratory.

Preparation of the Stock Standard Turbidity Solution

1. Solution-I Dissolve 1.000g Hydrazine Sulphate (Caution: Carcinogen: avoid inhalation, ingestion, and skin contact) $(NH_2)_2H_2SO_4$ in distilled water and dilute to 100ml. In a volumetric’ flask.
2. Solution-II Dissolve 10.00g Hexamine LR grade, (CH2)6 N4 in distilled water and dilute to 100 ml. in a volumetric flask.
3. In 100 ml. Volumetric flask, mix 12.5 ml. 501.1 and 12.5 ml. 501.11. Let them stand for 24 hours at 25 ±3°C, dilute to mark and mix. The turbidity of this suspension is 1000 NTU.
4. Prepare the solutions and suspension weekly.

Making the Dilutions for Different Ranges

Dilutions of other values can be prepared from this 400 NTU solution by the following successive dilution method:

Solution	1000 NTU Std.	Dist. Water
400 NTU	40ml.	60ml.
200 NTU	20ml.	80ml.
100 NTU	10ml.	90ml.

Calibration

1. Switch ON the instrument and keep it ON for some time.
2. Select appropriate range depending upon the expected turbidity of the sample.
3. Set zero of the instrument with turbidity free water using a blank solution & adjust 000 in the display with the ‘Set Zero’ Knob. The CAL Control should be moved by 5 turn anticlockwise from 0 positions.
4. Now in another test tube, take standard suspension just prepared as above. For 0-200 NTU range use 100 NTU solution and for higher range use 400 NTU solutions as standard.
5. Take its measurement and set the display to the value of the standard suspension with the Calibrate knob.
6. Now the instrument is ready to take measurement of any solution of unknown concentration.

Interference

i. Turbidity can be determined for any water sample that is free of debris and rapidly settling coarse sediments.
ii. Dirty glassware or the presence of air bubbles disturb the surface visibility of the sample & will give false results.
iii. “TRUE COLOUR” i.e. Water colour due to dissolved substances that absorb light causes measured turbidities to be lowest.
iv. This effect usually is not significant in the case of treated water.

Operation

1. Allow sufficient warm up period after switching ON the instrument.

Instrumental Chemistry

2. Take the test tube containing distilled water or blank solution in the Test Tube Holder and close the Test Tube Holder Lid. Make sure that the mark on test tube coincides with the mark on the panel. .

Please ensure that the appropriate range is selected.

3. Select the required range for measurement.
4. Adjust the display to 000 by adjusting 'Set Zero' knob.
5. Remove the test tube containing distilled water & insert another test tube containing standard solution (say 400 NTU). Place it in the test tube holder.
6. Take the measurement of the solution suspension & adjust the 'Calibrate' knob so that the display reads the selected standard solution value.
7. Again check the display zero with the test tube containing distilled water.
8. Now the instrument is ready to take measurement of any unknown suspension.

Precautions

1. Sample test tube must be thoroughly cleaned both inside and outside. In case the test tube gets scratched or etched, discard it.
2. Do not touch the test tube where the light strikes i.e. at the sides of the test tube. So hold the test tube only at the top end.
3. Fill the test tube with samples or standards which have been thoroughly agitated. Allow sufficient time for the air bubbles to escape otherwise the reading will slowly come down. When the readings are taken in the agitated state with air bubbles, the readings will be higher.
4. Please ensure that the mark on the test tube coincides with the mark on the instrument panel while taking the readings.
5. Do not take the refrigerated samples immediately after taking out from the refrigerator because they will frost the tube and also will damage the sensor, keep the samples for some time in the room temperature allow to defrost and then introduce into the instrument.

2

Total Dissolved Solids

Introduction

Total Dissolved Solids (often abbreviated TDS) is a measure of the combined content of all inorganic and organic substances contained in a liquid in: molecular, ionized or micro-granular (colloidal sol) suspended form. Generally the operational definition is that the solids must be small enough to survive filtration through a sieve the size of two micrometer. Total dissolved solids are normally discussed only for freshwater systems, as salinity comprises some of the ions constituting the definition of TDS. The principal application of TDS is in the study of water quality for streams, rivers and lakes, although TDS is not generally considered a primary pollutant (e.g. it is not deemed to be associated with health effects) it is used as an indication of aesthetic characteristics of drinking waterand as an aggregate indicator of the presence of a broad array of chemical contaminants.

Primary sources for TDS in receiving waters are agricultural and residential runoff, leaching of soil contamination and point source water pollution discharge from industrial or sewage treatment plants. The most common chemical constituents are calcium, phosphates, nitrates, sodium, potassium and chloride, which are found in nutrient runoff, general storm-water runoff and runoff from snowy climates where road de-icing salts are applied. The chemicals may be cations, anions,molecules or agglomerations on the order of one thousand or fewer molecules, so long as a soluble micro-granule is formed. More exotic and harmful elements of TDS are pesticides arising from surface runoff. Certain naturally occurring total dissolved solids arise from the weathering and dissolution of rocks and soils. TheUnited States

has established a secondary water quality standard of 500 mg/l to provide for palatability of drinking water.

Total dissolved solids are differentiated from total suspended solids (TSS), in that the latter cannot pass through a sieve of two micrometers and yet are indefinitely suspended in solution. The term “settleable solids” refers to material of any size that will not remain suspended or dissolved in a holding tank not subject to motion, and excludes both TDS and TSS. Settle able solids may include larger particulate matter or insoluble molecules.

Total dissolved solids (TDS) consists of minerals, organic matter, and nutrients that have dissolved in water - the ions and compounds that you cannot see in the water. Water is known as the universal solvent because of its ability to dissolve, to some degree, most elements and compounds. The major components of TDS of natural waters include: bicarbonate (HCO3-), calcium (Ca+2), sulfate (SO4-2), hydrogen (H+), silica (SiO4), chlorine (Cl-), magnesium (Mg+2), sodium (Na+), potassium (K+), nitrogen (N2, NH3, NO-2, NO-3), and phosphorus in the form of phosphate (PO4-3). The have been listed more or less in order from most concentrated to least concentrated in typical waterways. Bicarbonate can make up 50% of TDS in some streams. Minor constituents that are normally just a trace in streams include: iron (Fe+3), copper (Cu+2), zinc (Zn+), boron (B+3), manganese (Mn+2), and molybdenum (Mo+).

A constant level of these total dissolved solids is essential for the maintenance of aquatic life because the density of total solids determines flow of water in and out of an organism’s cells (osmosis). Plus the nutrients (nitrogen and phosphorus) are important for organism growth. A sudden or extreme change in TDS can be detrimental to aquatic life. For instance, an increase in salts could kill freshwater species whose bodies are not constructed to live in saltwater.

The natural sources of dissolved solids are rocks, bedrock, and soils. As water comes in contact with them, minerals will dissolve to some degree. Geologic settings that include limestone (calcium carbonate) and halite (salt, sodium chloride), which readily dissolve in water, generally have waters with high TDS values. Regions underlain by rocks not susceptible to weathering, such as quartz-rich granite, generally have waters with low TDS levels.

The hydrological setting also exerts a strong control on the amount of TDS. Groundwater generally has high TDS values because it moves slowly and comes in contact with lots of rocks and sediment. Conversely, storm water runoff has low TDS because it moves rapidly and has limited contact with rocks and sediments. Because of this relationship, TDS is typically highest in streams flowing during low flow conditions, when groundwater is the primary source of water. During high flow conditions, stream TDS is low because storm runoff is the primary source of water.

The greater the land area that water has to come in contact with soils and rocks, the more likely the TDS levels will be higher. For instance, if TDS levels were analyzed at the mouth of a stream that drained a 60 square mile watershed, they would higher than a sample taken from the mouth of a stream draining the upper 5 square miles of that same watershed.

The term total dissolved solids is often confused with other types of stream measurement tests. For instance, total solids (TS) is the sum of both TDS and visible solids (sediments) that would contribute to the turbidity of water. Total dissolved solids is also different than conductivity, which is a measure of the electrical conductance of water. Total dissolved solids measures the amount of ions in water, while conductivity measures those ions’ ability to do something - conduct electricity. Distilled water (very low TDS) has little capacity for electron conductivity. The more ions in the water, the higher the electron flow. Usually there is a strong correlation between conductivity and TDS, but there is still a difference between the two. Conductivity is only an approximate predictor of TDS. Salinity is also different than total dissolved solids. Salinity deals only with salts and is defined as the concentration of all ionic constituents that include halides, bicarbonates, and sodium chloride.

Total dissolved solids is a complex water quality parameter because it is directly linked to so many chemical and biological processes, and incorporates a number of the other water parameters that we test. The average concentration of total dissolved solids for the world’s rivers is 100mg/L, while North American rivers average 142.6 mg/L. Each region in the country has a specific, normal TDS level - some high, some low. Ecosystems are adjusted to local conditions; therefore, a large change in TDS concentrations will disrupt the

system and increase its overall sensitivity.

Human Impacts

Because total dissolved solids are related to so many other chemical parameters and processes, humans can increase TDS levels in a number of ways. Rain will wash additional dissolved solids into a stream. This will occur naturally but we can increase it by encouraging soil erosion through poor farming practices, construction sites, timbering, and removal of riparian zones. Soil can bring in more minerals, nutrients, and metals. Rain will also be more effective at dissolving minerals if it is acidic, and humans have drastically lowered the pH (increased acidity) of rainfall through car exhausts and the burning of fossil fuels. Rain can also wash excess nutrients into a stream if too much fertilizer is placed on cropland or lawns. Since nutrients are a component of TDS, any human practices that contribute nutrients to streams will increase TDS levels. See the Nitrogen and Phosphorus Information Sheets. An easy to understand dissolved solid - salt - is another common artificial source of higher TDS. Road salt used on roads in the winter can wash into waterways.

Measurement

The two principal methods of measuring total dissolved solids are gravimetry and conductivity. Gravimetric methods are the most accurate and involve evaporating the liquid solvent and measuring the mass of residues left. This method is generally the best, although it is time-consuming. If inorganic salts comprise the great majority of TDS, gravimetric methods are appropriate.

Electrical conductivity of water is directly related to the concentration of dissolved ionized solids in the water. Ions from the dissolved solids in water create the ability for that water to conduct anelectrical current, which can be measured using a conventional conductivity meter or TDS meter. When correlated with laboratory TDS measurements, conductivity provides an approximate value for the TDS concentration, usually to within ten-percent accuracy.

Hydrological Simulation

Hydrologic transport models are used to mathematically analyze movement of TDS within river systems. The most common

models address surface runoff, allowing variation in land use type, topography, soil type, vegetative cover, precipitation, and land management practice (e.g. the application rate of a fertilizer). Runoff models have evolved to a good degree of accuracy and permit the evaluation of alternative land management practices upon impacts to stream water quality.

Basin models are used to more comprehensively evaluate total dissolved solids within a catchment basin and dynamically along various stream reaches. The DSSAM model was developed by the U.S. Environmental Protection Agency (EPA). This hydrology transport model is actually based upon the pollutant-loading metric called "Total Maximum Daily Load" (TMDL), which addresses TDS and other specific chemical pollutants. The success of this model contributed to the Agency's broadened commitment to the use of the underlying TMDL protocol in its national policy for management of many river systems in the United States.

Practical Implications

High TDS levels generally indicate hard water, which can cause scale buildup in pipes, valves, and filters, reducing performance and adding to system maintenance costs. These effects can be seen in aquariums,spas, swimming pools, and reverse osmosis water treatment systems. Typically, in these applications, total dissolved solids are tested frequently, and filtration membranes are checked in order to prevent adverse effects.

In the case of hydroponics and aquaculture, TDS is often monitored in order to create a water quality environment favorable for organism productivity. For freshwater oysters, trouts, and other high value seafood, highest productivity and economic returns are achieved by mimicking the TDS and pH levels of each species' native environment. For hydroponic uses, total dissolved solids is considered one of the best indices of nutrient availability for the aquatic plants being grown.

Because the threshold of acceptable aesthetic criteria for human drinking water is 500 mg/l, there is no general concern for odor, taste, and color at a level much lower than is required for harm. A number of studies have been conducted and indicate various species' reactions range from intolerance to outright toxicity due to elevated TDS. The

Instrumental Chemistry

numerical results must be interpreted cautiously, as true toxicity outcomes will relate to specific chemical constituents. Nevertheless, some numerical information is a useful guide to the nature of risks in exposing aquatic organisms or terrestrial animals to high TDS levels. Most aquatic ecosystems involving mixed fish fauna can tolerate TDS levels of 1000 mg/l. The Fathead minnow (Pimephales promelas), for example, realizes an LD50 concentration of 5600 ppm based upon a 96 hour exposure. LD50 is the concentration required to produce a lethal effect on 50 percent of the exposed population. Daphnia magna, a good example of a primary member of thefood chain, is a small planktonic crustacean, about 0.5 millimeters in length, having an LD50 of about 10,000 ppm TDS for a 96 hour exposure.

Spawning fishes and juveniles appear to be more sensitive to high TDS levels. For example, it was found that concentrations of 350 mg/l TDS reduced spawning of Striped bass (Morone saxatilis) in the San Francisco Bay-Delta region, and that concentrations below 200 mg/l promoted even healthier spawning conditions. In the Truckee River, EPA found that juvenile Lahontan cutthroat trout were subject to higher mortality when exposed to thermal pollution stress combined with high total dissolved solids concentrations.

For terrestrial animals, poultry typically possess a safe upper limit of TDS exposure of approximately 2900 mg/l, whereas dairy cattle are measured to have a safe upper limit of about 7100 mg/l. Research has shown that exposure to TDS is compounded in toxicity when other stressors are present, such as abnormal pH, high turbidity, or reduced dissolved oxygen with the latter stressor acting only in the case of animalia.

Water Classification

Water can be classified by the amount of TDS per liter:

Fresh water < 1500 mg/L TDS

Brackish water 1500 to 5000 mg/L TDS

Saline water > 5000 mg/L TDS

Relation Between TDS, Turbidity and Electrical Conductivity

TDS (Total Dissolved Solids): TDS, in water treatment, is the inorganic residue left after the filtration of colloidal and suspended

solids and then the evaporation of a known volume of water. TDS is reported as ppm or mg/l. TDS, in RO design projections, is determined by calculation using the sum of the cations, anions and silica ions (with the ion reported "as such", not "as calcium carbonate"). Feed or permeate TDS, in RO design projections, can also be estimated by applying a conversion factor to the conductivity of the solution. TDS can also be determined in the field by use of a TDS meter. TDS meters measure the conductivity of the water and then apply a conversion factor that reports TDS to a known reference solution (e.g. ppm sodium chloride or ppm potassium chloride). The user is cautioned that TDS levels for waters with a mixture of ions and determined from conductivity measurements may not agree with TDS calculated as a sum of the ions. As a rough rule of thumb, one ppm of TDS (when referenced to a NaCl solution) correlates to a conductivity of two micromhos/cm (microSiemens/cm).

Turbidity: Turbidity is a suspension of fine colloidal particles that do not readily settle out of solution and can result in a "cloudiness". Turbidity is determined by a Nepholometer that measures the relative amount of light able to pass through a solution. Turbidity is reported as NTU (Nepholometric Turbidity Units). Typical RO element warranties list a maximum of 1.0 NTU for the feed water.

Fig. 3: Showing the TDS meter

Measurement of TDS by TDS Meter

TDS is generally measured by the help of TDS meters here, we shall be using a TDS meter of HANNA instruments these meters

Instrumental Chemistry

generally have a range of TDS normally the DIST NO1 is used in the measurement of TDS in drinking water and other water bodies. (see fig 3). It is very easy to use the top cover has a slide switch, slide it to ON and the display should read 000 and dip the meter upto the mark and read the TDS isn ppm.

3

Electrical Conductivity

Introduction

Digital Conductivity Meter is a solid state instrument design to provide the precise conductivity measurement. The instrument is ideal for monitoring salt contents in Natural Water, Drinking Water, Treated Water, Waste Water, Brine Solution, sea Water and soluble salt in solids. a multi-position selector switch quickly sets the digital display to the-desired test range. The LED display is easy to read even in the dark. The uses of the solid state I.C. circuitry make the model versatile and reliable. The instrument is extremely useful for agriculture and soil analysis laboratories, swimming pools, water quality control in boiler feed water, water works departments fertilizer plants, petroleum refineries, transport undertakings, breweries, textile plants, rayon & silk mills etc.

Theory

Electrical Conductivity is the ability of a solution to transfer (conduct) electric current. It is the reciprocal of electrical resistivity (ohms). Therefore conductivity is used to measure the concentration of dissolved solids which have been ionized in a polar solution such as water. The unit of measurement commonly used is one millionth of a Siemen per centimeter (micro-Siemens per centimeter or μS/cm). When measuring more concentrated solutions, the units are expressed as milli-Siemens/cm (mS/cm) i.e.- 10-3 S-cm (thousandths of a Siemen). For ease of expression, 1000 μS/cm are equal to 1 mS/cm. Often times conductivity is simply expressed as either micro or milli Siemens. However

this unit of measurement is sometimes (incorrectly) referred to as micro-mho's rather than micro-Siemens. The expression "mho" was simply the word ohm spelled backwards. Several means of conductivity expression have been adopted by various industries as a way of making the units of expression into whole numbers. The water softening industry refers to "grains" of hardness and uses TDS or total dissolved solids as a measurement scale. While TDS is really a gravimetric measurement, because in solution the solids are predominately present in ionic form, they can be approximated with conductivity. The TDS scale uses 2 μS/cm = 1 ppm (part per million as $CaCO_3$). It is also expressed as 1 mg/l TDS. While the method of measurement is the same, some conductivity meters can make the conversion and express the results of a measurement in many different units. This is helpful for users who are accustomed to one particular unit of measurement.

Principle of Operation

A Conductivity Cell in a measuring solutions is placed in the inverting input path of an 'Operational Amplifier' when AC voltage of constant amplitude and suitable frequency is applied to the system then for a given feedback resistance Rf. the output E0 is linearly proportional to the conductance of the solution i.e. G1. The conductance value is normally required to be multiplied by the cell constant to convert into Conductivity unless provision already exists in the' instrument to compensate for the same. This provision is made in the next part of the amplifier after conditioning is displayed on a 3% digit display. This indicates directly, the Conductivity of the solution under measurement referred to the reference measurement i.e. 25°C.

Conductivity of the Water

General water hardness is related to the dissolved minerals in the water. General hardness is a misleading term that is often confused with carbonate hardness or temporary hardness, which is actually related to alkalinity and relates to the "buffering capacity" of the water (its ability to resist pH changes). This means that if the carbonate hardness is high then the pH will be extremely stable or alternatively if the carbonate hardness is low the pH of the water

will be able to fluctuate easily. The term general hardness should be replaced with a simpler term: Hardness. Water hardness is the measurement of the amount of ions which have lost two electrons (divalent cations) dissolved in the tested water and is therefore, related to total dissolved solids. The more divalent cations dissolved in the water the "harder" the water. Generally the most common divalent cations are calcium and magnesium, however other divalent cations may contribute including iron, strontium, aluminum, and manganese. Typically the other divalent cations contribute little to no appreciable additions to the water hardness measurement. A stream or river's hardness reflects the geology of the catchment's area and sometimes provides a measure of the influence of human activity in a watershed. For example, sites that have active or abandoned mines nearby often have higher concentrations of iron ions in the water resulting in a very high hardness degree.

Water hardness can be expressed in many different units including French degrees, German degrees, Clark degree, grains per gallon, mg/L $CaCO_3$ (calcium carbonate), and ppm (parts per million). General conversions are below:

1 ppm = 1 mg/L $CaCO_3$
1 ppm = 0.058 grains/US gallon
1 ppm = 0.07 Clark degrees
1 ppm = 0.10 French degrees
1 ppm = 0.056 German degrees
1 French degree = 1 hydrotimetric degree
1 Clark degree = 1 grain / Imperial gallon as calcium carbonate
1 French degree = 1 part / 100,000 calcium carbonate
1 German degree = 1 part / 100,000 calcium oxide
1 grain/US gallon = 17.1 ppm
1 grain/US gallon = 1.20 Clark degrees
1 grain/US gallon = 1.71 French degrees
1 grain/US gallon = 0.958 German degrees

Relation Between the Conductivity and TDS (Total Dissolved Solids)

There is a relation between the TDS and the conductivity, the

TDS is directly proportional to Electrical conductivity of the liquid under test.

The chart below shows the relation between the TDS and the electrical conductivity. Can you measure water hardness with a *conductivity sensor* or *TDS sensor*? The answer is Yes, however it depends on the accuracy that you want to have in your measurement. In general the following table describes the water hardness as measured by a TDS, conductivity, or hardness measurement.

TDS(ppm)	Conductivity (uS/cm)	°f	Hardness
0-70	0-140	0-7	Very Soft
70-150	140-300	7-15	Soft
150-250	300-500	15-25	Slightly Hard
250-320	500-640	25-32	Moderately Hard
320-410	640-820	32-42	Hard
Above 410	Above 820	Above 42	Very Hard

Description of the Instrument

The technical specifications along with the picture (see fig 2)of the front panel is given below

Technical Specifications

Range: Mhos: 200 Micro Mhoms/cm to 1000mMhoms/cm inS range.

Accuracy: ±0.3% F.S. 200 Micro Mhoms to200m Mhoms/c.m.±1 % F.S. in last range 1000 Mhoms/cm.

Resolution: 0.1 Mhos Micro Mhoms/cm.

Measuring Frequency: 1000 Hz.

Temperature Compensation: 0 to 50°C.

Cell Constant: 0.4 to 1.6 adjustable.

Function Selector CHECK/ COND./ CELL CONST/CAL

For full scale adj. (at back panel)Function selector at CH ECK Position.

Digital Display: 3½ digit LED display

Power Supply: 220V± 10% 50 HzAC.

Dimensions: L27SxB 175xH 75mm.

Accessories

1. Conductivity Cell (Dip Type) 2. Operational Manual
3. Dust Cover

One. One. One.

FRONT PANEL CONTROLS (see fig 4)

Digital Display: 3½ digit LED display that reads COND value of any aqueous solution.

Function Switch: This is a 3 position switch.

1. In the COND position it measures total conductivity.
2. In the CHECK position the display will read 1.000
3. In CELL Constant. position, display reads cell constant value.

Cell Const: This control is used for cell Constant compensation (the value of the cell constant is printed on the conductivity electrode cell itself)

Back Panel Controls: ON/OFF switch: This switch is used to make the instrument On/off

Check: When function switch is at CHECK position adjust 1.000 on display by CAL control.

Input Connections: Two banana sockets at the back are the input of the instrument. The Conductivity ceUleads fitted with banana plugs isconnected to these banana sockets.

Fuse: 100 mA fuse is for current protection.

Calibration of the Instrument

The following procedure is to be adopted to CALIBRATE the instrument with measuring cell.

A. Take a standard solution of known Conductivity at 25°C in a beaker

Fig. 4: Showing the front panel of Electrical Conductivity Meter LT-16 (Labtronics)

and dip the cell into the solution.

B. Set the I RANGE' switch within range of the standard solution.

C. Switch the 'FUNCTION SWITCH' to the CHECK Position and see that display reads 1.000. If not, set it with [CAL] which at the back of the instrument.

D. Set the function switch to Conductivity position and bring the display to the reading corresponding to the known Conductivity by means of the CELL CONSTANT control. Check the cell constant value mark new cell constant. If it does not match the value on the Conductivity Cell. The instrument is calibrated & can be used to determine the Conductivity of unknown solution.

Conductivity Measurements

To measure the Conductivity of any solution proceeds as follows:

A. Rinse the cell with' solution whose Conductivity is to be measured.

B. Dip the Conductivity Cell in the solution under test.

C. Set the FUNCTION SWITCH to CHECK position.

D. Display must read 1.000, if not set it with CAL Control at the back panel.

E. Set the CELL CONSTANT control to the cell consistent value of the Conductivity Cell.

F. Set the FUNCTION switch to COND position.

G. Connect the Conductivity cell at the rear of the instrument.

H. Set the temp control to the actual temperature of the solution under test.

I. Bring the RANGE switch at a position where maximum resolution is obtained.

J. Read the display. This will be the exact conductivity at 25° C.

Preparation of the Conductivity Solution

Prepare a solution of sodium chloride 5.85gm/100ml double distilled water and that will read the electrical conductivity of 11.564mohms/cm

Cell Constant Verification

Checking the cell constant as per the following procedure is recommended before any measurement.

(A) Set the 'FUNCTION' Switch to CHECK Position and adjust the display to 1. 000.

(B) Dip the Conductivity Cell in the solution of known value and adjust the temperature control into the actual temperature of the solution.

(C) Move the 'FUNCTION' Switch to Conductivity Position and range switch to appropriate value.

(D) Adjust the cell constant knob so that the display reads the known value of the solution.

(E) Bring the FUNCTION switch to CELL CONST. position.

(F) The display shows the cell constant of the Conductivity Cell.

Care of Conductivity Cell

After the use the Conductivity Cell must be thoroughly washed or dipped in the distilled water. The cell may be washed by cleaning it in 90% detergent solution and scrubbing it with very fine brush. For more tenacious deposits. 2% solution of Hydrochloric Acid may be used. Utmost care must be kept so that the 'Plasticization' of the electrode is not damaged.

Conductivity Factor for Different Ions

Current is carried by both cations and anions, but to a different degree. The conductivity due to divalent cations is more than that of mono-valentcations. However, it is not true for anions. The conductivity factors for major ions present in water are listed below. Table below Conductivity Factors for ions commonly found in water.

Ion	**Conductivity Factor µS/cm per mg/L**
Cations	
Ca^{2+}	2.60
Mg^{2+}	3.82
K^{+}	1.84
Na+	2.13

Instrumental Chemistry

Anions	
$HC0_3$	0.715
CI	2.14
SO_4^{2-}	1.54
$N0_3$	1.15

4

Salinity

Introduction

Digital Salinity Meter is a solid state instrument designed to provide the precise conductivity measurement. The instrument is ideal for monitoring salt contents in Natural Water, Drinking Water, Treated Water, Waste Water, Brine Solution, Sea Water and soluble salt in soils. A multi position selector switch quickly sets the digital display to the desired test range. The LED display is easy to read even in the dark. The uses of the solid state I.c. circuitry make the model versatile and reliable. The instrument is extremely useful for agriculture and soil analysis laboratories, swimming pools, water quality control in boiler feed water, water works departments, fertilizer plants, petroleum refineries, transport undertakings, breweries, textile plants, rayon & silk mills etc.

Principal of Operation

A SALINITY Cell dipped in a measuring solution is placed in the inverting input path of an 'Operational Amplifier' when AC voltage of constant amplitude and suitable frequency is applied to the system then for a given feed back resistance R_f., the output E_0 is linearly proportional to the conductance of the solution *i.e.* G_1. The conductance value is normally required to be multiplied by the cell constant to convert into condo unless provision already exists in the instrument to compensate for the same. This provision is made in the next part of the amplifier after conditioning is displayed on a 3V2digit display. This indicate directly, the Salinity of the solution under measurement referred to the reference measurement i.e. 25°C.

Technical Specifications

Range	: 0.0 ppt to 50 ppt in 3 ranges
Accuracy	: I 0.5 % to Il digit.
Oscillator	: 1 KHz in built.
Temperature Compensation	: 0 to 50° C
Cell Constant adjt.	: 0.1 to 1.999 with digital display.
Function Selector	: CAL/SALINITY /CELL CONST.
CAL	: For full scale adj. (at back panel) at CAL Position

Function Selector

Digital Display Power Supply Dimension Weight

3'hdigit LED display. 220V I 10% HZ AC

L 275x B 175 x H 75 mm 2 Kg.

Accessories

1. Salinity Cell (Dip Type)
2. Operation Manual
3. Dust Cover

One One One

Front Panel Controls Digital Display (See Fig 5)

A 3½ digit LED display that reads Salinity value of any aqueous solution.

Function Switch

This is a 3 position switch.

Cell Constant

(1) In the Salinity position it measures total Salinity

(2) In the CAL position the display will read 1.000

(3) In CELL CONST. position, display reads cell constant value.

This control is used for cell constant compensation.

Back Panel Controls

ON/OFF: This switch is used to make the instrument On/Off.

CAL Control: When function switch is at CAL, Position adjust 1.000 on display by CHECK control.

Input Connections: Two banana sockets at the back are the input of the instrument. The Salinity cell leads fitted with banana

Fig 5: Showing the Front panel of the Salinity Meter Model LT -28 (LABTRONICS)

plugs is connected to these banana sockets.

Fuse: 100 mA fuse is for over current protection.

(1) Wash the Condo cell thoroughly with distilled water. (Before use the cell should be kept in distilled water for at least 24 hours/

(2) Fit the electrode leads to the input sockets at the rear of the instrument.

Calibration of the Instrument

The following procedure is to be adopted to CALIBRATE the instrument with measuring cell:

A. Take a standard solution of known Salinity at 25° C in a beaker and dip the cell into the solution.

B. Set the 'Range' switch within range of the standard solution.

C. Switch the 'FUNCTION SWITCH' to the CAL Position and see that the display reads 1.000 if not, set it with (CHECK) which at the back of the instrument.

D. Set the function switch to Salinity position and bring the display to the reading corresponding to the known Salinity by means of the CELL CONSTANT. Check the cell constant value. If it does not match the value marked on the cell. Please mark. new CELL CONST. value on the SALINITY cell. The instrument is calibrated & can be used to determine the SALINITY of unknown solution.

Salinity Measurements

To measure the SALINITY of any solution proceed as follows :¬

(a) Rinse the cell with solution whose Salinity is to be measure.

(b) Dip the SALINITY cell in the solution under test.

(c) Set the FUNCTION SWITCH to CAL position.

(d) Display must read 1.000, if not set it with CHECK Control at the back panel.

(e) Set the CELL CONSTANT control to the cell constant value of the Salinity Cell.

(f) Set the FUNCTION switch to SALINITY Position.

(g) Connect the SALINIIY cell at the rear of the instrument.

(h) Set the temperature control to the actual temperature of the solution under set.

(i) Bring the RANGE switch at a position where maximum resolution is obtained.

(j) Read the display. This will be the exact Salinity at 25° C.

Cell Constant Verification

1. Checking the cell constant as per the following procedure is recommended before any measurement:¬

2. Set the 'FUNCTION' switch to CAL position & adjust the display to 1.000.
3. Dip the Salinity cell in a solution of known value and adjust the temperature control into the actual temperature of the solution.
4. Move the FUNCTION switch to SALINITY. Position and range switch to appropriate value of the solution.
5. Adjust the cell constant knob so that the display reads the known value of the solution.
6. Bring the FUNCTION switch to CELL CONST. position.
7. The display show the cell constant of the Salinity cell.

Preparation of the Salinity Standard Solution

Prepare a 10ppt solution by dissolving 5.84 gm sodium chloride salt in 100ml of double distilled water

Care of Salinity Cell

After the use, the Salinity cell must be thoroughly washed or immersed in the distilled water. The cell may be washed by cleaning it in 90% detergent solution and scrubbing it with very fine brush. For more tenacious deposits, 2% solution of Hydrochloric acid may be used. Utmost care must be kept so that the 'Plantinization' of the electrode is not damaged.

Salinity of the Waters at a Glance

The specification of the standards are given in the appendix (WHO standards)

Salinity is the saltiness or dissolved salt content of a body of water.

- 35 g dissolved salt / kg sea water = 35 ppt = 3.5% = 35,000 ppm

Salinity in Water

- drinking water 100 ppm
- restriction on drinking water 500 ppm
- limit drinking water 1000 ppm
- limit agriculture irrigation 2000 ppm
- brackish water 500 - 30,000 ppm

- sea water 30,000 - 50,000 ppm
- brine > 50.000 ppm

Some more Facts About TDS Conductivity and Salinity

How is salinity measured? A quick way is to use a conductivity meter and read off the electrical conductivity. The idea being that a salty solution, because it is full of charged particles will conduct electricity. Most conductivity meters give readings in micro Siemens per cm (μS/cm).

So what's a micro Siemen? Well most fresh drinking water will have less than 100 μS/cm conductivity eg Melbourne. However in WA the statewide standard for drinking water is nearer 821 microS/cm. Some slightly salty drainage water found on salt affected farms in Victoria will be around 1800 μS/cm. In Western Australia salt drainage water conductivity could range from 8000 to 23000 microS/cm . Very brackish water could be around 27000 μS/cm. By the way seawater has conductivity of around 54000 μS/cm.

If you are growing salt sensitive crops make sure the conductivity is less than about 700 μS/cm. If your irrigation water is around 5000 μS/cm then make sure you are growing salt tolerant crops.

Sometimes just to confuse matters, conductivity is given in some textbooks in deci Siemens per meter (dS/m). The conversion is relatively easy 1 dS/m = 1000 μS/cm. Likewise if you come across milli Siemens per cm (mS/cm) just remember that 1 mS/cm = 1000 μS/cm.

Now some salinity meters read off parts per million (ppm). This is an approximation - the problem is that ppm is a measure of dissolved solids and its usually on a weight for volume basis. For example 50 ppm in water means there are 50 milligrams of solids per litre. How does a conductivity meter know how many ppm to show? It just uses its inbuilt conversion factor. This means that you need to choose a meter with either an appropriate factor or get one with an adjustable factor. Some meters display salts as ppt (parts per thousand). 1000 ppm = 1 ppt so that 4300 ppm = 4.3 ppt.

An open channel supplying towns and farms in the Mallee in Victoria. By the time this water gets to the Mallee from the Grampians it's conductivity is up to about 1100 μS/cm.

Salinity vs TDS. What's the connection? This is a commonly asked question. To answer it we have to delve into a little chemistry theory.

First the short answer

What's the connection between conductivity and TDS? TDS is more precisely measured in the laboratory by evapourating a measured sample gently to dryness then calculating how much solids are left. Conductivity is usually given as μS/cm which measures the ability of the sample to conduct an electric current.

There is no exact relationship between conductivity as μS/cm and TDS as ppm. So why are both measurements used? It has been discovered experimentally that for particular types of water there is an approximate relationship. In water with a higher proportion of sodium chloride to get to ppm just multiply the μS/cm reading by 0.5. For most other water for example in hydroponics solutions use a factor of 0.67 or 0.7 instead.

Sometimes it is useful to have some sort of comparison for values measured on a conductivity meter. Remember that conductivity of seawater is around 54000 μS/cm. This is approximately 35000 ppm TDS. Seawater has a high proportion of sodium chloride and this is around 28000 ppm.

Now the descrptive answer

Different salts in water have a different ability to conduct electricity. This is because of the differences in charge and size / weight and mobility of the different ions. This difference is quantified as a property called the specific conductance. The specific conductance is a value based on the theoretical conductivity of ions at very low concentrations. Although it is possible to calculate the conductivity for any electrolyte at any temperature and concentration, the exact contribution of individual ions is difficult to determine due to interactions between the ions. This means that it is difficult to work out what the conductivity of a particular salt mix should be, and hence it is difficult to establish the theoretical relationship between conductivity and TDS for a given mixture.

A simple experiment was carried out at Apps Laboratories. Three salt solutions all at the same concentration 0.01 mol/l were made up. There were sodium chloride NaCl, calcium chloride $CaCl_2$

and sodium bicarbonate $NaHCO_3$. Conductivity of the solutions was measured using the Labtronics LT-16 conductivity meter.

Salt (all 0.01 mol/l)	mg/l	Conductivity µS/cm	TDS factor - mg/l / Cond
NaCl	584	1156	0.51
$CaCl_2$	1110	2310	0.48
$NaHCO_3$	840	865	0.97

5

The pH

Now we are going to discuss the pH meter, which is the most important instrument used in a modern chemistry lab. pH is a very important parameter of all the chemical reagents and also water. Too Low pH makes the substance acidic and too high pH makes the substance alkaline and pH 7 makes the substance neutral. There is a definite pH value of the each and every substance. (see the pH scale) In this chapter we will see an instruction for the use of the digital pH meter model no MK VI (Systronix electronics)

The Description Of The Instrument

The instrument is very easy to handle, only a basic idea of operation is needed, the front panel (see fig 6)

The pH meter has a glass and a reference electrode (discussed in the chap 1 of tome 3 The Architecture of chemistry).

Fig 6: Showing the front panel of the pH meter MK-VI

The pH Electrode

The pH meter is provided with a reference glass electrode (the discussion is in chap 18 Tome 2 the Encyclopaedia of Inorganic chemistry).

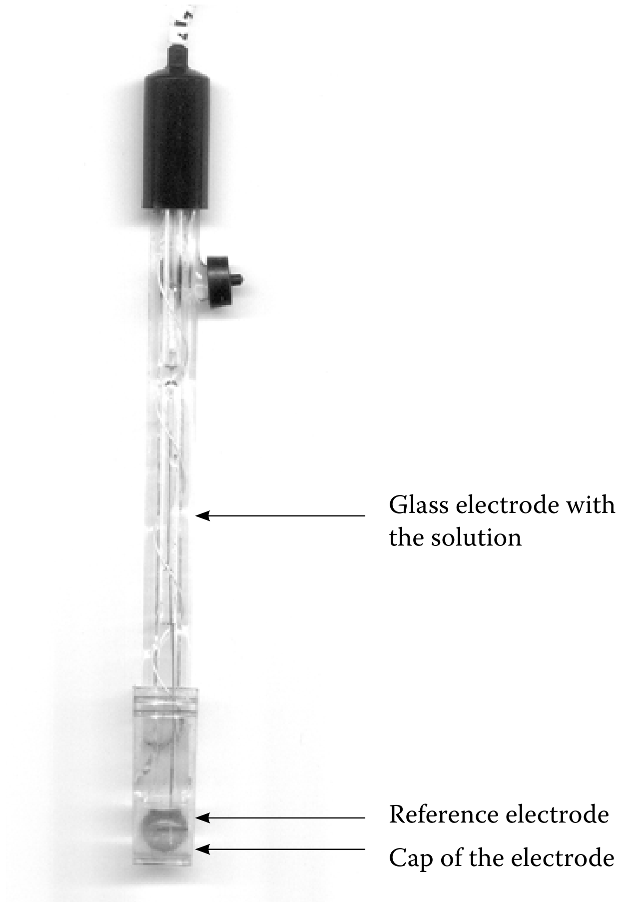


Fig. 7: Showing the actual size of the MK-IV electrode (No 2656)

Instruction Manual for Digital pH Meter Type MK- VI

Introduction

MK-VI is a precise and compact instrument using solid state devices for direct measurement of pH and millivolts. It is basically a voltage measuring device with added features. The high input

impedance and the stability of its measuring circuit enable it to make the chemical measurements with outstanding precision and reproducibility

Technical Specification

pH Range 0 -14 pH.

Millivolt range 0 to 1999 mV

Resolution 0.01 pH; 1 mV.

Repeatability: 0.01 pH: 1 digit; & 1 mV +1 digit in mV mode

Input Impedance 5 × 1011

Temperature Compensation. 0- 100°C (Manual).

Display. 4 digit LED with automatic polarity and decimal indications

Power 230 V, 50 Hz. A.C.

Supplied accessories One set of standard glass/ reference or Combine electrodes with stand, Clamp Two batters and instruction manual

Panel Features

(a) *Power 'ON' (rear panel)*: Switches on/off the mains supply to the unit

(b) *Digital Display*: A four digit display for reading pH and mV with auto decimal and polarity indications

(c) *Function Selector*: A three position selector Switch for selection of the desired mode of measurement i. e. mV, pH, CHECK

(d) *Standardise/set pH (Calibration)*: In pH mode it sets the digital readout to the value of the standard buffer, e. g. 7.0 pH. in mV mode it is used for zero adjustment.

(e) *Manual Temperature °C*: This control, compensates for the temperature characteristic of measuring electrodes and operates in pH mode only.

(f) *SLOPE* : Provides slope correction for pH electrodes Socket for connecting.

(9) *G. E. (rear panel)*: The glass electrode (--pH electrode) to the unit

(h) *R. E. (rear panel)*: Socket for connecting the reference

Instrumental Chemistry

(--colomel electrode) to the unit.

Operating Procedure

The instrument is designed with the aim that it should be very simple in operation. It does not involve any special techniques for measurement and is simpler than other conventional pH meters. Connect the instrument to 230 V a. c. mains, having good earthling; switch on the supply

Before use, keep the pH electrode dipped in distilled water for at least 24 hours and maintain it as per instruction given in the manual as well separately with the pH electrode. Never touch the lower sensitive bulb of the electrode by hand or rough material, Always use cotton or tissue paper/filter for drying the electrodes.

pH Measurement

Connect the electrodes to the pH meter. Prepare 7 pH and 4.0 or 9.2 pH buffer solution using buffer tablets . Wash the electrodes with distilled water and dry it with tissue paper. Dip the electrodes in 7 pH buffer solution. Keep Temperature knob at 25°C position Set the function switch to pH position The meter will give some reading near 7.0 pH, Say it gives 6.8 Use STANDARDISE control to make the reading exactly 7.00 Remove the 7.00 pH Solution. Wash and dry the electrodes as instructed earlier Take 4.0 pH buffer solution and dip the electrodes in it. See the Digital Display, say it reads 4.3 pH The error is 0.3 pH. Now use the SLOPE control (on backside of the instrument) to adjust the pH reading 4.00 pH. The meter is now standardised and hence does not disturb any control.

To measure the pH of an unknown solution. Immerse the electrodes in that solution and directly read its pH value. Of course, every time the electrodes must be washed and dried as instructed above during idle/electrode-clearing period, keep the function selector in CHECK position

Millivolt Measurement

Millivolt measurements corresponding to the pH of the solutions can be made by simply flicking the function selector from the pH position to mV position For using the unit as a general purpose millivoltemeter, initially, short circuit the G.E. and R.E. sockets and then adjust the STANDARDISE control for zero read out. Thereafter

connect the signal through the G.E. and R.E. sockets.

How to Use 'Check'

After standardisation of the unit with a known buffer solution, place the function Switch in CHECK and read the display along with the polarity. Note this reading on a paper. After a series of pH measurements if one wants to ensure that the buffer setting / standardisation is undisturbed or in the event of accidental movement of STANDARDISE control, all one has to do is to put the unit in CHECK mode and the read- out. If the reading is different from the one noted earlier, it should be set right by the STANDARDISE control. Thus the unit stands calibrated without reusing the buffer solutions.

Maintenance of Electrodes

1. Shake the electrodes gently, to ensure that the internal buffer solution covers the whole membrane and no air bubblier are entrapped.
2. Reference/ combination electrodes should be filled with the appropriate electrolyte (Saturated KCl Solution upto a height of about 1 cm below the filling hole.
3. Wash off any salt film present on the exterior of reference / combination electrode, using distilled water
4. To ensure pressure equalisation, in calomel electrode. The stopper of the electrolyte opening may be removed during operation.
5. Soak the electrodes in water for some hours (preferable overnight), before using first time, Otherwise also keep the electrodes dipped in distilled water when not in use.
6. Electrodes which have a slow response due to drying out of the membrane or use under extreme conditions may be re-activated by soaking in 0.1 N hydrochloric acid for several hours.

Instrumental Chemistry

6

Dissolve Oxygen

Introduction

Oxygen is the most abundant element of the earth's crust and waters combined. It is the single most important component of surface water for self-purification processes and the maintenance of aquatic organisms which utilize aerobic respiration.

The combination of the divalent oxygen atom with single valent hydrogen atom comprises the extremely stable H_2O molecule. Under natural conditions water exists in several physical states, but the molecule itself dissociates to a very limited extent as ions (H+ and OH-). Two OH- molecules can, by covalent bonding, combine to form H_2O_2 or hydrogen peroxide.

The double bonded, two-atom molecule is the single form of oxygen which has relevance to this discussion. Air contains approximately 20.9 percent oxygen gas by volume; however, the proportion of dissolved oxygen in air dissolved in water is about 35 percent, because nitrogen (the remainder) is less soluble in water. Oxygen is considered to be moderately soluble in water. This solubility is governed by a complex set of physical conditions that include atmospheric and hydrostatic pressure, turbulence, temperature and salinity .

In British Columbia surface waters, dissolved oxygen levels are usually high, close to saturation levels, and often greater than 10 mg/L. The amount of oxygen in marine water is naturally about 20% less than in freshwater. In lakes, oxygen levels depend primarily on seasonal temperature variation, depth, and trophic status.

Oxygen Cycles and Monitoring Frequency

Dissolved oxygen cycles in productive waters are common, and site-specific details must be taken into account when designing a sampling strategy. Diurnal oxygen fluctuations typically result in sub-optimal conditions for at least brief periods, therefore the timing of measurements is very important. It is the intent of two-number criteria proposed that these fluctuations do not go lower than the instantaneous minimum criterion. In natural waters influenced by oxygen generation from primary production, daily cycles usually are sinusoidal with a maximum concentration reached late in the day and a minimum concentration in early morning. Whether a cycle exists naturally or is the result of a manipulated discharge (e.g., a hypolimnetic withdrawal from a reservoir), it is necessary to determine a reasonable average of the extreme high and low concentrations once the shape of the oxygen curve is determined (i.e., at least two measurements must be taken). Cycles are more likely to be non-sinusoidal in manipulated flows, and the USEPA recommends that time-weighted averages be used in these circumstances. In addition, maximum dissolved oxygen concentrations used in calculating daily averages should not exceed the known saturation limit.

The required frequency of sampling can be based on a number of circumstances (e.g., known variability of oxygen levels in the source water, the most sensitive species / life stages present and their duration, and logistical constraints such as cost or distance between sample sites). For normal ambient monitoring, five measurements taken weekly within 30 days is a minimum frequency. As mentioned earlier, daily average values have to be used where cycles exist. Additional sampling is recommended where ambient levels are known to vary over time or are close to criteria values. A few excursions below the mean can easily result in non-attainment. In such cases, additional sampling over a 7-day averaging period would be prudent to check for anomalies and determine the extent of low dissolved oxygen concentrations.

Temperature Considerations

Although it was decided there were insufficient data to incorporate a temperature component into broad aquatic life criteria, it should be recognized that the effects of hypoxia likely are more

severe under the added stress of higher temperatures. If the presence of early life stages (prone to highest mortality) coincides with high seasonal summer temperatures, special attention should be given to the attainment of criteria.

Multiple Toxicity Considerations

The dissolved oxygen criteria are sufficiently conservative so that multiple toxicity generally will not be a cause for concern. With the exception of ammonia, there is limited opportunity in the literature to develop quantitative relationships between dissolved oxygen and potential toxicants. It is recommended that multiple toxicity be dealt with on a site-specific basis where, in the presence of known contaminants (e.g., cyanide, un-ionized ammonia), the criteria for dissolved oxygen and the other contaminants may have to be modified to provide the appropriate level of protection for aquatic life. Where literature studies lack sufficient detail to accomplish this, bioassays could be performed on sensitive local species for the range of expected conditions.

Interstitial Considerations

It is incumbent on resource managers to have a reasonable understanding of the aquatic life resources being protected. For example, in salmonid-bearing waters, embryos and alevins typically are buried in the stream bottom or shallow lake bed for several months each year. Due to the variety of salmonids endemic to British Columbia, there may only be a limited time that early life stages are not present in spawning media. As discussed previously, the criteria for early life and mature life stages are the same when interstitial measurements are being used for the buried early life stages. If surface water is being tested, a 3 mg/L differential is assumed, wherein the instantaneous minimum and mean criteria values are raised to 9 and 11 mg/L, respectively, for the buried early life stages. Interstitial data clearly represent a more direct measure of available oxygen; however, the increased complexity of sampling may not be practical for routine field monitoring.

Natural Oxygen Levels That Do Not Meet Criteria

Studies of dissolved oxygen levels in spawning media have

Instrumental Chemistry

determined that, under normal circumstances, concentrations may not meet provincial criteria. Typical survival rates of incubating salmonids from egg deposition through to emergence are known to be relatively low due to a combination of stressors, and lack of oxygen commonly is cited. Based on works which detail the elevated oxygen requirements near the time of hatch, it is apparent that hypoxic stress, particularly in the interstitial environment, is not uncommon during early development.In cases where natural dissolved oxygen concentrations in surface waters or sub-surface waters do not meet criteria, no statistically significant reduction below natural levels should be permitted. An accurate determination of natural ambient conditions, including temporal variability, would be critical in such an assessment. Statistical comparison of background levels (e.g., for lakes) or upstream / downstream measurements in relation to a perturbation such as a discharge should use a one-tailed, two-sample t-test, at the 0.05 probability level. The minimum sampling requirement is five measurements collected weekly in 30 days. The two-sample t-test requires the different stations to have similar variances (use the F-test). If, at the affected site, data from a discharge event are pooled with steady-state data, the variance may increase and become dissimilar to the ambient site invalidating the two-sample t-test. Data from the steady state and the event should be treated independently to reduce variance.

Dissolved Oxygen

The air we breathe contains about 20% oxygen. Fish and other aquatic organisms require oxygen as well. The term Dissolved Oxygen (DO or D.O.) refers to the amount of free oxygen dissolved in water which is readily available to respiring aquatic organisms. State water quality standards often express minimum concentrations of dissolved oxygen which must be maintained in order to support life as well as be of beneficial use. Levels of dissolved oxygen below 4-5 milligrams per liter affect fish health and levels below 2 milligrams per liter can be lethal to fish. Additionally, biochemical oxygen demand (BOD) is commonly used with reference to effluent discharges and is a common, environmental procedure for determining the extent to which oxygen within a sample can support microbial life. The test for BOD is especially important in waste water treatment, food

manufacturing, and filtration facilities where the concentration is crucial to the overall process and end products. High concentrations of DO predict that oxygen uptake by microorganisms is low along with the required break down of nutrient sources in the medium.

Basic Principles of Polagrography Cell:

Liquid and Air state of equilibrium is reached when the partial pressure of oxygen, i.e. the part of the total pressure that is due to oxygen, is equal in air and in liquid. The liquid is then saturated with oxygen

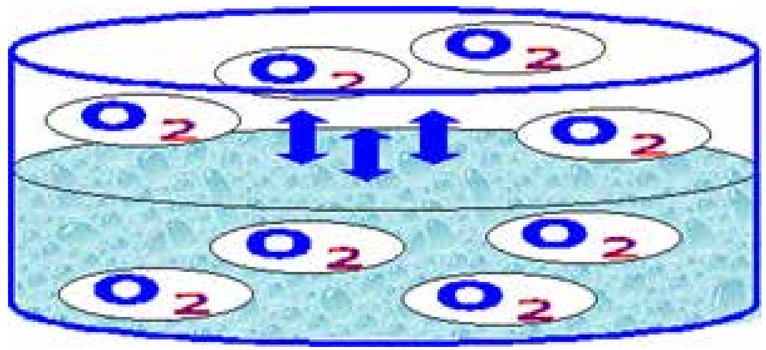


Fig. 8: Air and liquid oxygen equilibrium

Measuring Principle of Dissolved Oxygen Meter

Dissolved oxygen can be measured with membrane-type dissolved oxygen electrodes using a galvanic cell or membrane-type dissolved oxygen electrodes using a polarograph.

(1) Membrane-type dissolved oxygen electrodes using a galvanic cell—The membrane-type dissolved oxygen electrodes using a galvanic cell are configured as illustrated below. The working electrode uses a noble metal (Ag), and the opposite electrode uses a base metal (Pb). For the electrolyte, an alkaline solution is used. For the membrane, a highly oxygen-permeable Teflon membrane is used. Oxygen which has passed through the membrane is reduced with the working electrode. A reduction current in proportion to the concentration of the dissolved oxygen is generated, and then the dissolved oxygen is measured.

(2) Membrane-type dissolved oxygen electrodes using a polarograph The membrane-type dissolved oxygen electrodes using a polarograph are configured as illustrated below. The working electrode uses a noble metal (Pt), and the opposite electrode uses Ag. For the electrolyte, a potassium chloride solution is used, and for the membrane, a Teflon membrane is used. Voltage is applied between the two electrodes so that the threshold diffusion current for oxygen is generated there. The oxygen which has passed through the membrane is reduced with the working electrode. A reduction current in proportion to the dissolved oxygen is generated, and then the dissolved oxygen is measured.

In either case, the current which has flowed in proportion to the concentration of the dissolved oxygen is processed with the current amplifier, and then the concentration of the dissolved oxygen is measured.

Polargram:

When an electrode of noble metal such as platinum or gold is made 0.6 to 0.8 V negative with respect to a suitable reference electrode such as AgAgCl or an calomel electrode in a neutral KCI solution (see Figure 9), the oxygen dissolved in the liquid is reduce at the surface of the noble metal.

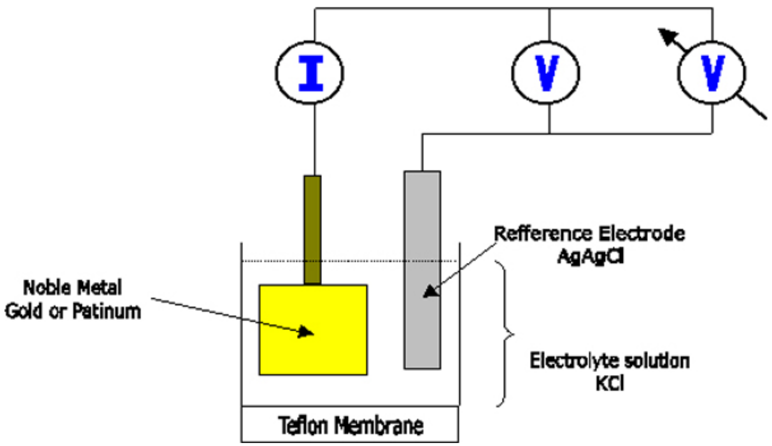


Fig. 9: Polarographhy diagram

This above phenomenon can be observed from a current to voltage diagram called a polarogram of the electrode. As shown in Figure 10, the negative voltage applied to the noble metal electrode (called the cathode) is increased, the current increases initially but soon it becomes saturated. In this plateau region of the polarogram, the reaction of oxygen at the cathode is so fast that the rate of reaction is limited by the diffusion of oxygen to the cathode surface. When the negative bias voltage is further increased, the current output of the electrode increases rapidly due to other reactions, mainly, the reduction of water to hydrogen. If a fixed voltage in the plateau region (for example, - 0.6V) is applied to the cathode, the current output of the electrode can be linearly calibrated to the dissolved oxygen (Figure 1.3b). It has to be noted that the current is proportional not to the actual concentration but to the activity or equivalent partial pressure of dissolved oxygen, which is often referred to as oxygen tension. A fixed voltage between -0.6 and -0.8 V is usually selected as the polarization voltage when using Ag/AgCl as the reference electrode or any other EID's dissolved oxygen electrodes. Additionally for physical and chemical correctness, partial pressure in a liquid actually refers to the fugacity. In the pressure range relevant to the measurements at hand, it is acceptable to equate the two values and this allows us to restrict the following considerations to the partial pressure. In dry, atmospheric air, the partial pressure of oxygen is 20.95% of the air pressure. This value is reduced over a water surface because water vapor has its own vapor pressure and a corresponding partial pressure.

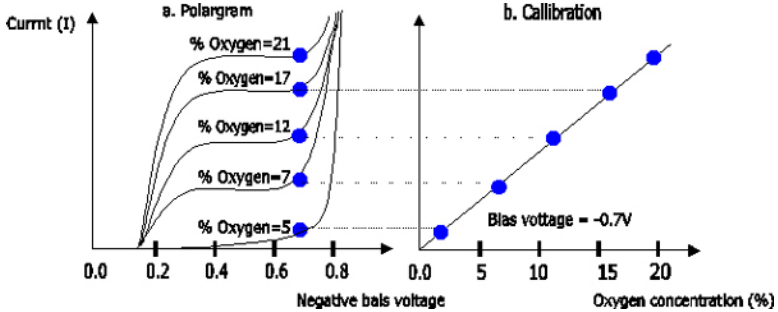


Fig. 10: (a) Current to voltage diagram at different oxygen tension; (b) Calibration obtained at a fixed polarization voltage of -600 mV.

When the cathode, the reference electrode, and the electrolyte are separated from the measurement medium by a polymer membrane, which is permeable to the dissolved gas but not to most of the ions and other species, and when most of the mass transfer resistance is confined in the membrane, EID's electrode system can measure oxygen tension in various liquids. This is the basic operating principle of the membrane covered polarographic Dissolve oxygen probe (Figure 11).

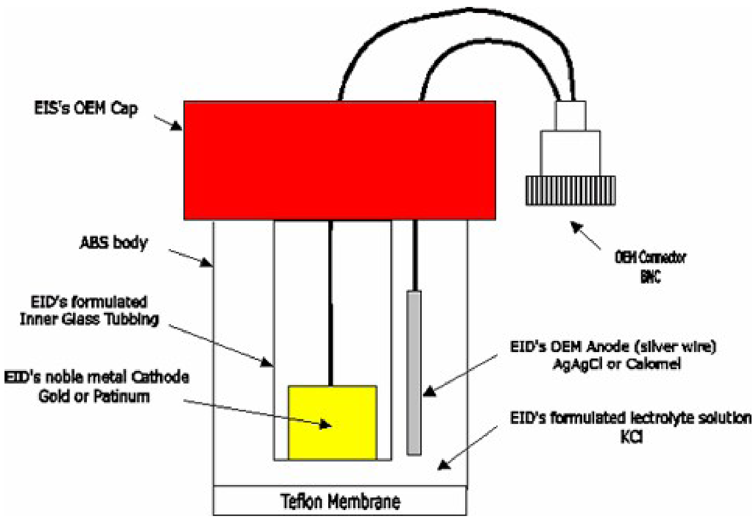


Fig. 11: Basic Polarographhy electrode

The basic principle underlying the electrochemical determination of oxygen concentration is the use of membrane covered electrochemical sensors. The main components of the sensors are the oxygen permeable membrane, the working electrode, the electrolyte solution and a possible reference electrode. A voltage is applied between the gold (platinum or silver) cathode and the anode that consists of either lead or silver (AgAgCl), and causes the oxygen to react electrochemically. The higher the oxygen concentration the higher the resulting electric current. The current in the sensor is measured and, after calibration, converted into the concentration of dissolved oxygen. If the anode is made of silver, the meter applies the required voltage (polarographic sensor). If it is made of lead, the sensor is self-polarizing, i.e. the voltage is generated in the sensor

by the electrodes themselves, comparable to the process in a battery (galvanic sensor). The meter merely evaluates the current.

Electrode Reactions

For our polarographic electrodes, the reaction proceeds as follows:

Cathodic reaction: $0_2 + 2H_20 + 2e- \rightarrow H_2O_2 + 2OH-$

$H_20_2 + 2e- \rightarrow 20H-$

Anodic reaction: $Ag + Cl- \rightarrow AgCl + e-$

Overall reaction: $4Ag + 0_2 + 2\,H_2O + 4\,Cl- \rightarrow 4\,AgCl + 4\,OH-$

The reaction tends to produce alkalinity in the medium together with a small amount of hydrogen peroxide.

Number of Electrons Involved

Two principal pathways were proposed for the reduction of oxygen at the noble metal surface. One is a 4-electron pathway where the oxygen in the bulk diffuses to the surface of the cathode and is converted to H_2Ovia H_2O_2 (path a in Fig. 1.6). The other is a 2-electron pathway where the intermediate H_2O_2 diffuses directly out of the cathode surface into the bulk liquid (path b in Figure 1.6). The oxygen reduction path may change depending on the surface condition of the noble metal. This is probably the cause for time-dependent current drift of polarographic sensors. Since the hydroxyl ions are constantly being substituted for chloride ions as the reaction starts, KCI or NaCl has to be used as the electrolyte. When the electrolyte is depleted of Cl-, it has to be replenished.

$$2e^{-} \rightarrow (a) \rightarrow H_2O_2$$

$$O_2 \rightarrow O_2 \xrightarrow{2e^{-}} H_2O_2$$

$$diffusion$$

$$\rightarrow (a) \rightarrow H_2O_2$$

Equation showing the alternative pathway of oxygen reduction at cathode surface

Calibration

Calibration must be carried out for dissolved oxygen measurements on a regular base. This is because the measuring

process consumes the electrolyte solution in the sensor head, as shown by the electrode reactions presented above. The ions of the electrolyte solution bind the released metal ions, thereby changing the composition of the solution. The recommended calibration period depends on the oxygen sensor used and ranges from one week for pocket instruments to 1-2 months. Each linear calibration function is defined by at least two points. For dissolved oxygen measurements with EID meter and/or logger, one of the points on the line is the zero point of the sensor. At the zero point, the sensor signal obtained in the absence of oxygen lies below the resolution of the sensor. This point is called the zero-current point of the sensor. The second point

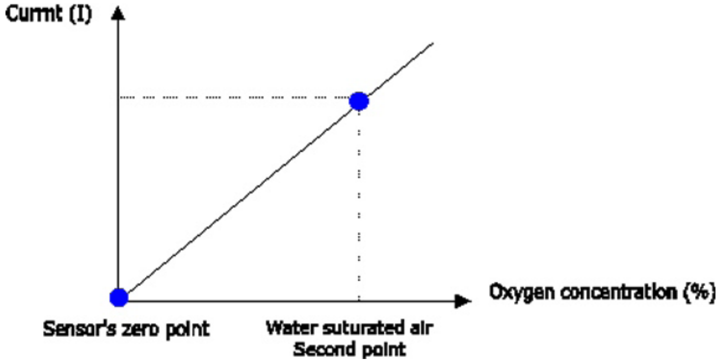


Fig. 12: Two-point calibration

of the calibration line can be set as required. Its position is based on the fact that, in a state of equilibrium, the partial pressure of oxygen in liquid and air is equal.

The rate at which oxygen enters a dissolved oxygen probe is a function of:

- the concentration of oxygen in the sample
- the diffusion coefficient/permeability of the membrane (function of temperature)

As described above calibration routines for dissolved oxygen probes use a two point linear calibration where one point is at zero mg/L oxygen and the second point is at saturation or equilibrium with the atmosphere, C*. The zero measurement is not zero volts due to the conductivity of the electrolyte between the electrodes as well as any errors in the analog signal conditioning circuit. For

the circuit and probe system used in the Environmental lab the zero measurement is approximately 1 mV (where approximately 200 mV corresponds to saturation levels of oxygen) and hence the zero measurement is not significant. Thus a single point calibration is used.C* is a function of the atmospheric pressure and temperature. The functional relationship with temperature is implemented using a lookup table (based on equilibrium at atmospheric pressure) with interpolation. The effect of atmospheric pressure is implemented as shown (Equation 1 below).

$$C^* = \frac{\rho}{\rho_{atm}} f(T)$$

The permeability of the membrane increases about 5% per C degree. I chose to use 25 C as the reference temperature and thus $K_{membrane}$ (Tref) has a value of 1. The following (equation 2) creates a coefficient that describes this variation.

$$K_{membrane}(T) = K_{membrane}(T_{ref})e^{0.05(T-T_{ref})}$$

The slope of the linear fit (k) can be calculated after the voltage corresponding to saturation oxygen is measured (Equation 3 below).

$$C = \frac{C^* K_{membrane}}{V * cal}$$

The slope coefficient is placed in the polynomial array.

The equation for the dissolved oxygen concentration illustrates that the predicted concentration is a function of sample temperature because $K_{membrane}$ varies with temperature. The coefficient, k, should be independent of temperature but will vary as a membrane fouls (Equation 4 below)

$$C = \frac{KV}{K_{membrane}}$$

Pressure

The constituents of air have been well defined, and it is known that air contains 20.946% oxygen. Since the total pressure in the air is the sum of all of the partial pressures (Dalton's Law), an atmospheric pressure of 760 millimeters Mercury (mmHg) in dry air will contain

a partial pressure of oxygen (pO2) of approximately 159 mmHg (760 mmHg * 0.20946). Changes in atmospheric pressure will cause a directly proportional change in the partial pressure of oxygen in the air. Atmospheric pressures will vary depending upon altitude and local weather conditions. Some average pressures for varying altitudes are listed in Table 1 bellow. The relationship between oxygen partial pressure and total atmospheric pressure should be understood and incorporated into the air calibration in order to minimize calibration error, which could be as high as 5-10% dependent upon altitude and local weather conditions. Most dissolved oxygen meters that have any sort of advanced air calibration (such as temperature compensation, which will be discussed in a later section) will be based upon an atmospheric pressure of 760 mmHg. Most tables of oxygen solubility are referenced to this value. Because of the change in oxygen partial pressure with changes in atmospheric pressure, a correction must be made when the pressure varies from this value. A simple means of incorporating pressure changes is listed in the "correction factor" shown in Table 1 bellow. The value listed is a rough multiplier, which can be used once the initial oxygen concentration is determined based upon temperature and relative humidity. A more accurate calculation for incorporating pressure will be discussed after relative humidity and temperature effects are investigated. Some EID's dissolved oxygen meters contain a pressure sensing device which provides compensation for pressure effects when an air calibration is performed. If you use our electrode on not-EID-meter, since most meters do not have this, it is usually necessary to note the average pressure in the local vicinity of the probe, which will be mostly altitude-based, and adjust the calibration using the simple correction factor or the more complex calculation performed later. A mercury barometer located in the immediate vicinity of the meter will give a relatively accurate measurement of the local atmospheric pressure if an older meter with no pressure sensor is used.

Table 1: Oxygen Value Corrected for Pressure (25 °C)

Altitude (ft)	Pressure (mm Hg)	Correction Calibration Correction Factor
-540	775	1.02
Sea Level	760	1
500	746	0.98
1000	732	0.96
1500	720	0.95
2000	707	0.93
2500	694	0.91
3000	681	0.9
3500	668	0.88
4000	656	0.86
4500	644	0.85
5000	632	0.83
5500	621	0.82
6000	609	0.8

Relative Humidity and Temperature Effect and Temperature Compensation

If desired the Eid's probes can be coupled with a temperature thermistor (10K Ohms) to achieve temperature compensation since $K_{membrane}$ varies with temperature. The discussion of pressure effects were based upon atmospheric pressure with dry air (no moisture content). Whenever air contains a certain amount of moisture, the atmospheric pressure contains another source of partial pressure—water vapor. If a comparison of the oxygen partial pressure in air with 100% relative humidity and air with 0% relative humidity is done while both are at the same atmospheric pressure, the air with 100% relative humidity will have a lower oxygen partial pressure due to the presence of the water vapor pressure (pH_2O). Water vapor pressure in air varies with temperature, and is well defined. The effect of temperature on oxygen partial pressure in moist air is such that higher temperatures yield lower oxygen partial pressure, while lower temperatures yield higher pressures. Note that the effects of relative humidity and temperature can cause errors when air calibration is performed in dry air, since most of the current tables and meter temperature compensations are based on air containing 100% relative humidity. Table 2 bellow shows both the oxygen concentration, which is linear with the partial pressure of oxygen, that would be present at 100% relative humidity and 0% relative humidity. The values only differ by a few percent in ambient air conditions, and thus is generally ignored.

Instrumental Chemistry

Most dissolved oxygen meters have temperature compensation for air at 100% relative humidity, and no manual correction is necessary. However, many older meters do not have temperature compensation included, and therefore this calculation must be done manually. If temperature is not compensated for in the calibration, the error can be as much as 20 to 30 % for every 10 degrees difference from 25 °C, and therefore temperature compensation is standard on most dissolved oxygen meters today. Since the effects of relative humidity is minimal at all but the highest temperatures, no current dissolved oxygen meters incorporate any kind of relative humidity sensing device. In order to ensure an accurate temperature and current reading, the probe must be exposed to the air for enough time to allow thermal equilibrium to occur. There are often significant temperature differences between the process water and the ambient air. Larger temperature gradients between the two necessitate additional time for thermal equilibrium to take place. For instance, a 20 °C difference between ambient air and process water can cause a calibration delay of about 30 minutes in many probes for the probe to fully equilibrate to ambient temperature. Since most temperature gradients will not be this large, allowing approximately 15 minutes is usually a safe assumption. It is common for users to calibrate the unit before the dissolved oxygen meter is reading the stabilized temperature and current value, which can cause significant error since a difference of even 5 °C from actual can cause the reading be off by 5 to 10%. It is often useful to have a calibrated temperature sensor, accurate to 1 °C or better, at the calibration location to know when the probe temperature is reading the correct ambient air temperature. It is useful to have an equation which can be used to determine oxygen concentrations in air based upon temperature, relative humidity, and pressure. Since the full equation is quite lengthy and complex, two easier versions are presented to the user, along with Table 2 bellow, to determine the correct oxygen concentration in air. Equation 5 bellow should be used with air with 100% relative humidity, and Equation 6 should be used for air with 0% relative humidity.

Equation 5 (100% Relative Humidity): $OS = (OS') * (P - p) / (760 - p)$

where:

OS= Oxygen solubility at barometric pressure of interest

OS'= Oxygen in saturation at one atmosphere (760 mmHg) at a given temperature

P= Barometric pressure of interest

p= Vapor pressure of water at the temperature of interest

Measurement of Dissolve Oxygen

The measurement of dissolve oxygen was previously done by the Winkler's Titration which is very time consuming and the availability of the sodium biiodate is very scarce. So in modern labs the dissolve oxygen meter is used for these measurements.

In this chapter we are going to discuss the LEUTRON DO-5509 model for the measurement of the dissolve oxygen. This instrument is very easy to handle and also convenient to carry.

Specifications of the Dissolve Oxygen Meter Do-5509

SPECIFICATIONS	
Sensors	The polarographic type probe with an incorporated temperature sensor.
Display	13 mm (0.5") LCD, 3 1/2 digits.
Measurement & Range	0 to 20.0 mg/L.
Resolution	0.1 mg/L.
Accuracy *(23 5 ℃ after calibration)*	0.4 % mg/L.
Sensor Temp. Compensation	Automatic from 0 to 40 ℃.
Panel adjust knob	ZERO knob, Calibration knob.
Battery	006P DC 9V battery (heavy duty).
Power Consumption	Approx. DC 3.5 mA.
Operating Temperature	0 ℃ - 50 ℃ (32 °F - 122 °F).
Operating Humidity	Less than 80% RH.
Size	*Main instrument :* 131x70x25 mm (5.2x2.8x1.0 inch).
	Oxygen probe : 125 mm x 20 mm dia.(4.9" x 0.8" dia.)
Weight	260 g (0.57 LB) * *Instrument with probe & battery.*
Accessories Included	Oxygen sensor probe........ 1 PC. Operation manual........ 1 PC. Spare Diaphragm (5 PCs per pack) OXDP-02........ 1 set. Probe-filling Electrolyte OXEL-03........ 1 set.
Optional Accessories	Oxygen probe (for DO-5509) ....OXPB-09 Spare Diaphragm (5 PCs per pack) ....OXDP-02 Probe-filling Electrolyte ....OXEL-03 Hard Carrying Case, (260 mm x 195 mm x 65 mm) ....CA-06 Soft Carrying Case, (190 mm x 90 mm x 55 mm) CA-03

* Appearance and specifications listed in this brochures are subjected to change without notice. C101100

OPRATION OF THE INSTRUMENT (See fig of the instrument)

Fig. 13: Showing the Dissolve Oxygen Meter DO-5509 and its electrode

1. Power on the instrument (it runs on a 9v HI watt battery)
2. Connect the probe to the multi-pin plug connector
3. Remove the cap form the electrode
4. Unscrew the membrane cap
5. Fill it with the Dissolve Oxygen electrolyte (OXEL-03)
6. The meter should come down to 000 reading slowly
7. Slide the DO-CAL switch to CAL position
8. Read the oxygen level
9. Turn the CAL screw with the screw driver to 20.9 level in the display

10. Slide the DO-CAL switch to DO position and allow the display reading come down to 000 position
11. Now the Meter is ready to work.
12. After use do not forget to turn off otherwise the battery will go flat

Testing of Biological Oxygen Demand by Dissolve Oxygen Meter

Biochemical Oxygen Demand (BOD) refers to the amount of oxygen that would be consumed if all the organics in one liter of water were oxidized by bacteria and protozoa (ReVelle and ReVelle, 1988).

The first step in measuring BOD is to obtain equal volumes of water from the area to be tested and dilute each specimen with a known volume of distilled water which has been thoroughly shaken to insure oxygen saturation. After this, an oxygen meter is used to determine the concentration of oxygen within one of the vials. The remaining vial is than sealed and placed in darkness and tested five days later. BOD is then determined by subtracting the second meter reading from the first. The range of possible readings can vary considerably: water from an exceptionally clear lake might show a BOD of less than 2 ml/L of water. Raw sewage may give readings in the hundreds and food processing wastes may be in the thousands.

Background Information

Microorganisms such as bacteria are responsible for decomposing organic waste. When organic matter such as dead plants, leaves, grass clippings, manure, sewage, or even food waste is present in a water supply, the bacteria will begin the process of breaking down this waste. When this happens, much of the available dissolved oxygen is consumed by aerobic bacteria, robbing other aquatic organisms of the oxygen they need to live. Biological Oxygen Demand (BOD) is a measure of the oxygen used by microorganisms to decompose this waste. If there is a large quantity of organic waste in the water supply, there will also be a lot of bacteria present working to decompose this waste. In this case, the demand for oxygen will be high (due to all the bacteria) so the BOD level will be high. As the waste is consumed or dispersed through the water, BOD levels will begin to decline. Nitrates and phosphates in a body of water can contribute to high BOD levels. Nitrates and phosphates are plant nutrients and can cause plant life

and algae to grow quickly. When plants grow quickly, they also die quickly. This contributes to the organic waste in the water, which is then decomposed by bacteria. This results in a high BOD level.

When BOD levels are high, dissolved oxygen (DO) levels decrease because the oxygen that is available in the water is being consumed by the bacteria. Since less dissolved oxygen is available in the water, fish and other aquatic organisms may not survive.

Test Procedure

The BOD test takes 5 days to complete and is performed using a dissolved oxygen test kit. The BOD level is determined by comparing the DO level of a water sample taken immediately with the DO level of a water sample that has been incubated in a dark location for 5 days. The difference between the two DO levels represents the amount of oxygen required for the decomposition of any organic material in the sample and is a good approximation of the BOD level.

1. Take 2 samples of water
2. Record the DO level (ppm) of one immediately using the method described in the dissolved oxygen test.
3. Place the second water sample in an incubator in complete darkness at 20oC for 5 days. If you don't have an incubator, wrap the water sample bottle in aluminum foil or black electrical tape and store in a dark place at room temperature (20oC or 68 °F).
4. After 5 days, take another dissolved oxygen reading (ppm) using the dissolved oxygen meter
5. Subtract the Day 5 reading from the Day 1 reading to determine the BOD level.
6. Record your final BOD result in ppm.

What to Expect

BOD Level *(in ppm)*	Water Quality
1 - 2	**Very Good** There will not be much organic waste present in the water supply.
3 - 5	**Fair: Moderately Clean**
6 - 9	**Poor: Somewhat Polluted** Usually indicates organic matter is present and bacteria are decomposing this waste.
100 or greater	**Very Poor: Very Polluted** Contains organic waste.

7

Mellting Point Boiling Point

Introduction

Determining the melting point of a compound is one way to test if the substance is pure. A pure substance generally has a melting range (the difference between the temperature where the sample starts to melt and the temperature where melting is complete) of one or two degrees. Impurities tend to depress and broaden the melting range so the purified sample should have a higher and smaller melting range than the original, impure sample.

Principle For Determination

The (fig 14) shows a Fisher-Johns melting point apparatus. This type of melting point apparatus uses small round, glass coverslips.

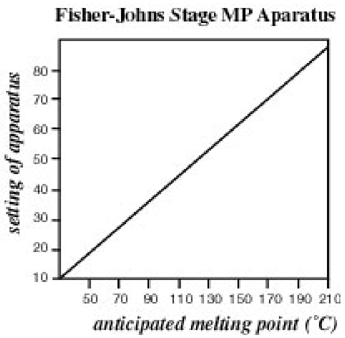
Fig. 14 & 14a: Showing the Fisher-Johns melting point apparatus (14a revised model) holes of thermometer and capillary

Using the Apparatus and Technique for Taking A Melting Point

1. Place a small amount of crystals on a coverslip.
2. Place a second coverslip on top.
3. Place the compound-coverslip sandwich on the round heating block.
4. Look through the lens above the heating block. Follow the directions given below to determine an appropriate heating rate
5. When done, place the used coverslips in the used coverslip recycling jar behind the instrument.
6. The aluminum cylinder is used to quick-cool the heating block between uses. Simply move the lens out of the way and place it on the round heating block when you are finished.

The rate of temperature increase in the vicinity of the melting point must be small, about 2°C per minute. This insures that the temperature of the hot plate, thermometer, and sample will be in thermal equilibrium. Increase the temperature rapidly at first and then slowly as the melting point is approached in the following manner:

1. Set the heating control at 100.
2. When the temperature is about 15 degrees below the anticipated melting point, change the setting to that indicated on the graph below.
3. Observe the crystals through the lens and record the temperatures at which melting begins and at which the last crystal disappears.
4. If you do not know the melting point of a compound, first take a crude melting point by heating rapidly. Then cool the plate to 20° below the crude melting point by placing the aluminum cylinder on it, and proceed to take a more careful melting point on a second sample of the compound.



The reference of the melting points and the boiling points are available in the CRC hand book[1].

8

Refractive Index

Introduction

A refractometer measures the extent to which light is bent (i.e. refracted) when it moves from air into a sample and is typically used to determine the index of refraction (aka refractive index or n) of a liquid sample.

The refractive index is a unitless number, between 1.3000 and 1.7000 for most compounds, and is normally determined to five digit precision. Since the index of refraction depends on both the temperature of the sample and the wavelength of light used these are both indicated when reporting the refractive index:

$$n_D^{20} \ 1.3742$$

The italicized n denotes refractive index, the superscript indicates the temperature in degrees Celsius, and the subscript denotes the wavelength of light (in this case the D indicates the sodium D line at 589 nm).

The refractive index is commonly determined as part of the characterization of liquid samples, in much the same way that melting points are routinely obtained to characterize solid compounds. It is also commonly used to:

- Help identify or confirm the identity of a sample by comparing its refractive index to known values.
- Assess the purity of a sample by comparing its refractive index to the value for the pure substance.
- Determine the concentration of a solute in a solution by comparing the solution's refractive index to a standard curve.

Theory

The speed of light in a vacuum is always the same, but when light moves through any other medium it travels more slowly since it is constantly being absorbed and reemitted by the atoms in the material. The ratio of the speed of light in a vacuum to the speed of light in another substance is defined as the index of refraction (aka refractive index or n) for the substance.

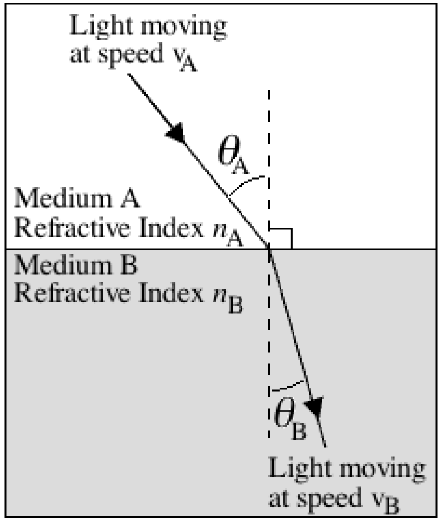


Fig. 15: Light crossing from any transparent medium into another in which it has a different speed, is refracted, i.e., bent from its original path (except when the direction of travel is perpendicular to the boundary). In the case shown, the speed of light in medium A is greater than the speed of light in medium B.

$$\text{refractive index } (n) \text{ of substance} = \frac{\text{speed of light in a vacuum}}{\text{speed of light in substance}} \quad \text{(Eqn 1)}$$

Whenever light changes speed as it crosses a boundary from one medium into another its direction of travel also changes, i.e., it is refracted (Figure 1). (In the special case of the light traveling perpendicular to the boundary there is no change in direction upon entering the new medium.) The relationship between light's speed in the two mediums (vA and vB), the angles of incidence (qA) and

refraction (qB) and the refractive indexes of the two mediums (nA and nB) is shown below:

$$\frac{v_A}{v_B} = \frac{\sin\theta_A}{\sin\theta_B} = \frac{n_B}{n_A} \quad \text{(Eqn 2)}$$

Thus, it is not necessary to measure the speed of light in a sample in order to determine its index of refraction. Instead, by measuring the angle of refraction, and knowing the index of refraction of the layer that is in contact with the sample, it is possible to determine the refractive index of the sample quite accurately. Nearly all refractometers utilize this principle, but may differ in their optical design.

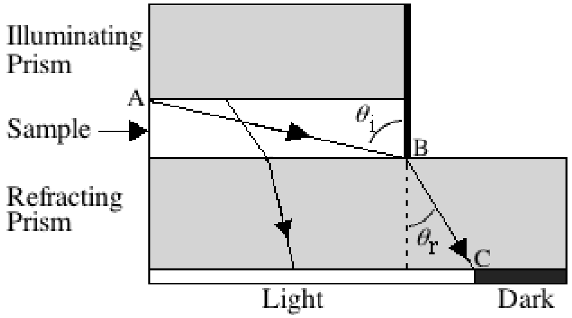


Fig. 16: Cross section of part of the optical path of an Abbe refractometer. The sample thickness has been exaggerated for clarity.

In the Abbe' refractometer the liquid sample is sandwiched into a thin layer between an illuminating prism and a refracting prism (Figure 2). The refracting prism is made of a glass with a high refractive index (e.g., 1.75) and the refractometer is designed to be used with samples having a refractive index smaller than that of the refracting prism. A light source is projected through the illuminating prism, the bottom surface of which is ground (i.e., roughened like a ground-glass joint), so each point on this surface can be thought of as generating light rays traveling in all directions. Inspection of Figure 2 shows that light traveling from point A to point B will have the largest angle of incidence (qi) and hence the largest possible angle of refraction (qr) for that sample. All other rays of light entering the refracting prism will have smaller qr and hence lie to the left of point

C. Thus, a detector placed on the back side of the refracting prism would show a light region to the left and a dark region to the right.

Samples with different refractive indexes will produce different angles of refraction (see Equation 2 above and recall that the angle of incidence and the refractive index of the prism are fixed) and this will be reflected in a change in the position of the borderline between the light and dark regions. By appropriately calibrating the scale, the position of the borderline can be used to determine the refractive index of any sample. In an actual Abbe' refractometer there is not a detector on the back of the refracting prism, and there are additional optics, but this is the essential principle.

(It is also possible to design a refractometer based on the reflection of light from the boundary between the prism and the sample. These types of refractometers are often used for continuous monitoring of industrial processes.)

In most liquids and solids the speed of light, and hence the index of refraction, varies significantly with wavelength. (This variation is referred to as *dispersion*, and it is what causes white light moving through a prism to be refracted into a rainbow. Shorter wavelengths are normally refracted more than longer ones.) Thus, for the most accurate measurements it is necessary to use monochromatic light. The most widely used wavelength of light for refractometry is the sodium D line at 589 nm.

If white light were used in the simple Abbe' refractometer optics shown in Figure 2, dispersion would result in the light and dark borderline being in different places for different wavelengths of light. The resulting "fuzziness" of the borderline would make precise work impossible. However, many Abbe' refractometers are able to operate satisfactorily with white light by introducing a set of "compensating prisms" into the optical path after the refracting prism. These compensating prisms are designed so that they can be adjusted to correct (i.e., compensate for) the dispersion of the sample in such a way that they reproduce the refractive index that would be obtained with monochromatic light of 589 nm, the sodium D line.

As mentioned earlier, the speed of light in a substance is slower than in a vacuum since the light is being absorbed and reemitted by the atoms in the sample. Since the density of a liquid usually

decreases with temperature, it is not surprising that the speed of light in a liquid will normally increase as the temperature increases. Thus, *the index of refraction normally decreases as the temperature increases* for a liquid (Table 1). For many organic liquids the index of refraction decreases by approximately 0.0005 for every 1 °C increase in temperature. However for water the variation is only about -0.0001/°C.

Many refractometers are equipped with a thermometer and a means of circulating water through the refractometer to maintain a given temperature. Most of the refractive index measurements reported in the literature are determined at 20 or 25 °C.

Operation of the Bausch & Lomb Abbe-3L Refractometer

1. Some labs store the refractometer with a piece of tissue in the prism assembly to keep the prism glass from being scratched. Open the prism assembly and remove the tissue.
2. Use a pipet to apply your liquid sample to the prism, being careful not to let the glass pipet tip touch the prism since this may scratch the soft prism glass. Add enough sample to achieve a thin film across the whole prism, typically 3 to 4 drops.
3. Close the prism assembly and turn on the lamp using the switch on the left side. (On some models the switch may be in the power cord.) Adjust the lamp so the light shines on the prism and look through the eyepiece.
4. If you are close to the index of refraction of your sample you should see that the view in the eyepiece shows a dark region on the bottom and a lighter region on the top. If you do not see a light and a dark region, turn the handwheel on the right side of the instrument until you do.
5. Before making the final adjustment, it will usually be necessary to adjust the lamp position and to sharpen the borderline between the light and the dark regions using the compensator dial on the front of the refractometer.
6. Once you have a crisp demarcation between the light and dark regions, turn the handwheel on the right hand side to place this borderline exactly on the center of the crosshairs.

7. To read the index of refraction, depress the switch on the left hand side of the refractometer until you see the scale through the eyepiece. The upper scale indicates the index of refraction. By carefully interpolating you can read the value to 4 decimal place accuracy.
8. Record the refractive index in your lab notebook. Then read the thermometer and record the temperature.

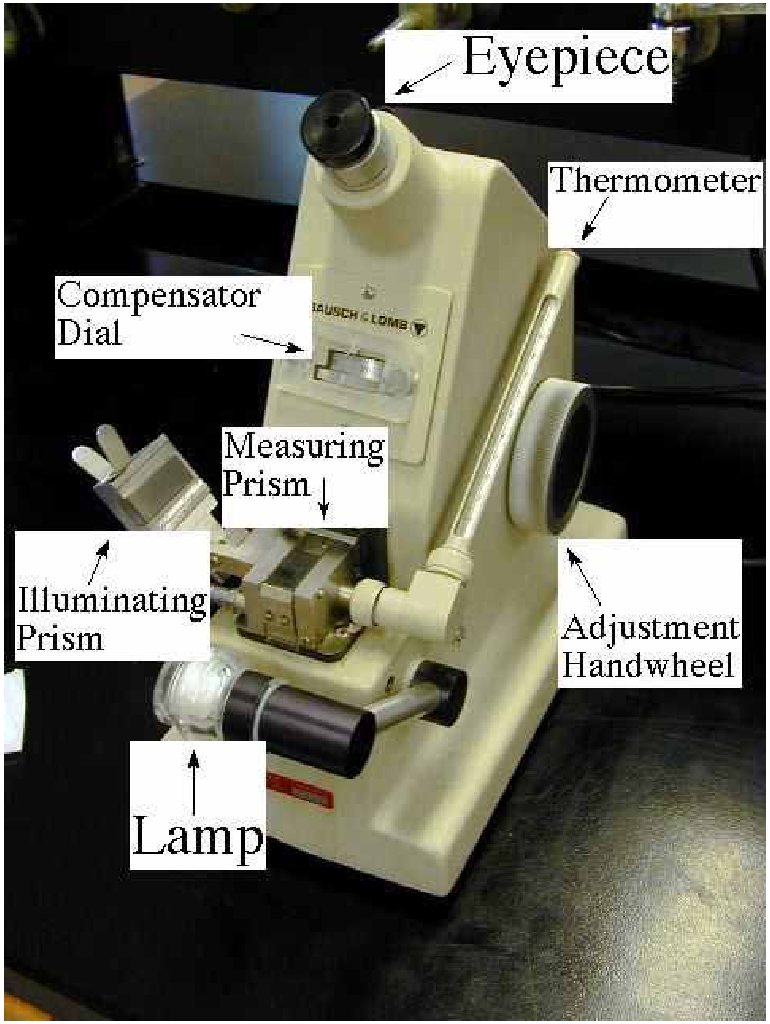


Fig. 17: Showing the the Bausch & Lomb Abbe-3L Refractometer

9. After you are finished, clean the refractometer. First use a tissue to dab away most of your sample. Then wash the prism with a little solvent, we usually use a simple alcohol such as ethanol for cleaning organic samples. A dabbing motion rather than a rubbing motion is preferred to minimize the chances of scratching the prism.
10. After you have finished cleaning the prism, place a clean tissue in the assembly. Before you leave make sure that the light has been turned off.

Detail Description of the Refractometer

Eyepiece

This is where you look to observe the reflection borderline and the instrument's scale.

Reflection Borderline

While looking through the eyepiece you adjust the reflection borderline (the borderline between light and dark regions) up and down using the Adjustment Handwheel until the borderline is exactly on the center of the crosshairs as shown below.

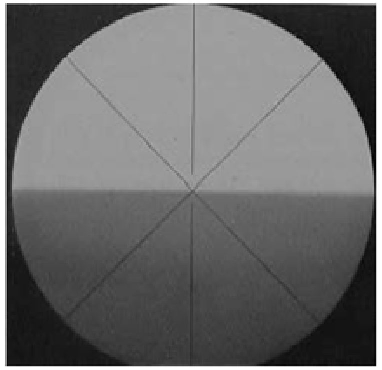


Fig 17A: Looking through the eye piece shows the reflection broad line

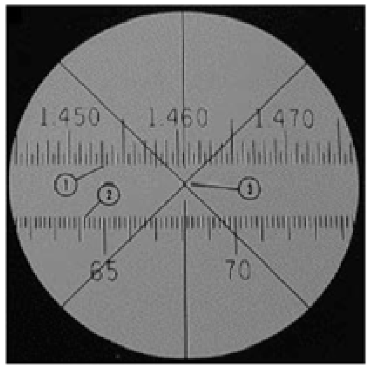


Fig 17B: Showing the Scale

Scale

When you look through the eyepiece you normally see the Reflection Borderline. But when you depress the scale switch you will be able to read the index of refraction from the scale as shown below.

Where the vertical crosshair intersects the upper scale is the index of refraction. In the example below the refractive index is 1.4606.

Compensator Dial

This dial is adjusted to give a sharp reflection borderline. When the compensator dial is properly set the reflection borderline will not have any color at the crosshairs, and will be faintly red at one end and faintly blue at the other. The Compensator Dial is protected by a cover that should be replaced when the dial is not being used.

Adjustment Hand wheel

This Handwheel is rotated to bring the reflection borderline seen through the eyepiece onto the center of the crosshairs.

Lamp

This lamp provides illumination to the upper illuminating prism. It is attached via a movable arm so that it can be adjusted to give optimum illumination.

Measuring Prism

Two to four drops of the sample are placed on this prism. (Enough to provide a thin film over the whole prism when the illuminating prism is closed over the sample.)

Illuminating Prism

After the sample is added, the illuminating prism is closed over the sample. The lamp is then adjusted so that light passes through this prism, through the sample, and into the measuring prism.

Thermometer

The refractive index of a sample changes with temperature. Thus the refractometer is equipped with a thermometer so that you can note the temperature at which your reading was taken.

On/Off and Scale Display Switch

On this model the On/Off (power) switch turns on the lamp, and when further depressed it displays the scale reading. On other models the On/Off switch may be located on the power cord, and the Scale Display switch is then a button (in approximately the same location as the switch on this model) that you depress in order to display the scale.

Tissue

A tissue is sometimes stored in the refractometer when not in use. This tissue should be removed before adding your sample.

Hand Held Refractometers

Different models of traditional MISCO refractometers have different internal scales on which to read fluid concentrations. Some instruments have specialized scales that indicate the exact mixture of the sample being tested, while others have an arbitrary unit of measure that works like a shorthand for refractive index measurements.

The instruction manual that comes with each refractometer carefully explains the procedure for comparing refractometer readings to the actual known concentrations or properties of your specific fluid. Trained MISCO technical support engineers are always available to assist you at any time.

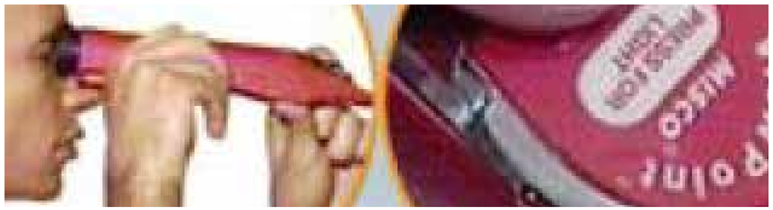
The new MISCO Digital Fiberoptic Refractometer has hundreds of available scales that display precise physical properties for specific fluids. It is no longer necessary to make conversion tables or charts for each of your fluids.

MISCO refractometers are easy-to-use and require little or no training. They can be mastered by ANYONE in just minutes.

Place a drop of sample on the measuring surface beneath the View Point Illuminator.

Look through eyepiece and press the View Point Illuminator.

Take your reading at the point where the contrast line (difference between light and dark areas) crosses the scale.



Need more information? Frequently Asked Questions

How it All Works

Light passing through a liquid is slowed compared to the speed

it travels in air. So once a fluid sample is placed on the measuring surface of a refractometer, the light passing through it slows and is bent.

The refractometer focuses this bent light on a tiny internal scale. The scale is magnified by the eyepiece lenses so it is easily visible.

The optics are supported by a bi-metal strip that moves lenses in response to temperature changes, ensuring that readings are accurate regardless of temperature.

Temperature is one of the single most important factors

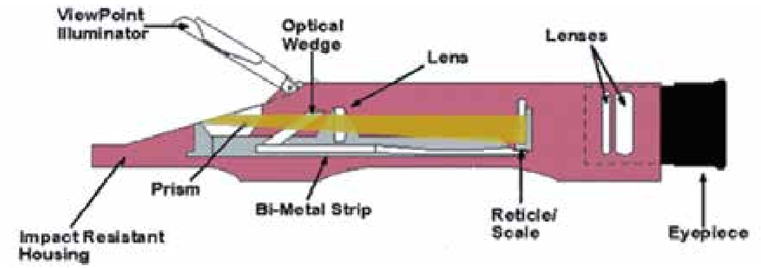


Fig. 19: Showing The schematic diagram of a hand held refractometer

What is a hand held Refractometer?

Fig. 20: Showing an actual Hand held refractometer

A refractometer is a relatively inexpensive yet essential piece of test equipment used by vineyard managers and winemakers. The rugged exterior of metal, rubber and plastic protects the highly polished optical glass, mirrors and prisms that are contained within. Once the sample is in place underneath the daylight plate, the winemaker can see the percentage Brix reading by looking through the monocular / eyepiece and reading the scale that is seen when he or she holds the refractometer in natural light.

What Does A hand held Refractometer Do, and How Does It Work?

As previously stated, a refractometer allows the winemaker to figure the percentage Brix (the relative "sugar weight" of a sample compared to distilled water) of the juice of grapes or other fresh fruit. Brix is sometimes referred to as Balling - don't worry, the terms are interchangeable. Depending upon the readings observed, a wine maker can monitor the progress of ripening and adjust his/her plans for harvest, if necessary. In simplest terms, the refractometer works much like a prism. Remember how, as a child, you could use a prism to separate out the different wavelengths of light (red, orange, yellow, green, blue, indigo, violet) when a source of light was shone on the prism at the correct angle? Well, the modern refractometer works on the same principle - it reacts differently to light (by giving a reading on a scale) depending upon the amount of sugar that is available in the liquid sample held between the daylight plate and the main prism assembly.

How to Calibrate and Use Your Refractometer

Before you start taking readings, it's very important to calibrate the refractometer. Some refractometers require the use of a special calibration liquid to perform this task, while others (like the ones sold at grapestompers.com) are calibrated with distilled water.

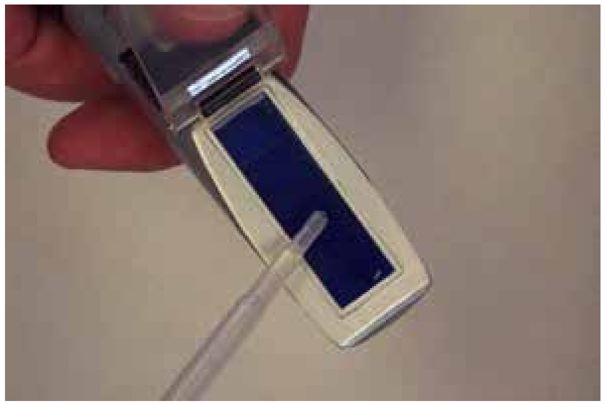


Fig. 20A: Putting the sample in the ref ractometer

Begin the calibration of your refractometer by lifting up the daylight plate and placing 2-3 drops of distilled water on top of the prism assembly. Close the daylight plate so the water spreads across

the entire surface of the prism without any air bubbles or dry spots.

Allow the test sample to sit on the prism for approximately 30 seconds before you attempt calibration in the next step. This allows the sample to adjust to the ambient temperature of the refractometer.

Hold the refractometer in the direction of a natural light source and look into the eyepiece. You will see a circular field with graduations down the center. You may have to focus the eyepiece to clearly see the graduations. Figure 1 (below) shows what you would see if you looked through the refractometer without any sample present.

Fig. 20B: Taking the reading of the refractometer

Turn the calibration screw (see photo at left) until the boundary between the upper blue field and the lower white field meet exactly at ZERO on the scale.

See example (Figure 2, shown below) of the interior view you'll see when you look through the eyepiece of the refractometer.

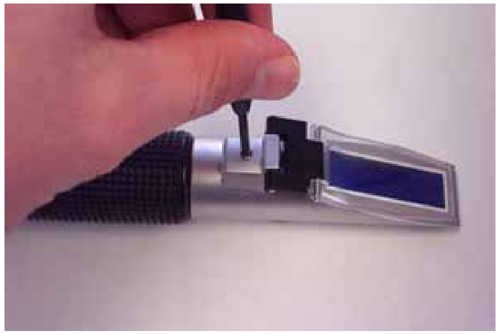


Fig. 20C: Calibrating the refractometer

Once the refractometer has been properly calibrated, you are ready to take readings of grape juice or whatever else you want to sample. Put away the calibration screwdriver. Clean the instrument (both the daylight plate and the top of the main prism assembly) using a soft, damp cloth, then place 2-3 drops of the desired sample on top of the prism. Close the daylight plate and take your reading as before.

Figure 3 (see below) illustrates what you might see at this point.

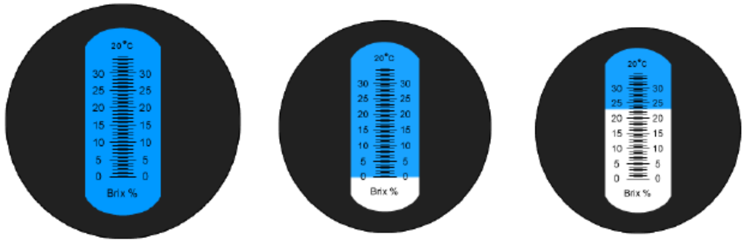


Fig. 20D a, b, c: Showing the Brix scale of the refractometer

The image to the left illustrates what the winemaker would see if he looked through the refractometer without any sample at all fig 20Da

Notice how the entire scale is colored blue; no white at all.

When looking through the monocular, be sure you are using natural light to view the readings; you should not read a refractometer in the prescence of fluorescent light.

This is what the chemist sees once he has properly calibrated the refractometer. fig 20Db

Notice that the reading is taken where the blue and the white meet. Calibrate to ZERO using distilled water as the sample.

If your refractometer does not automatically compensate for the temperature of the sample, you must take this into account or your readings will be off.

Finally, we get to sample. 20Dc

As you can see, this sample is reading 23% Brix.

Be sure to cleanse and dry the refractometer before putting it away in storage.

Warnings and Maintenance of Your Refractometer

Accurate measurement depends on careful calibration. Follow the instructions above closely. A reminder: Differences between the ambient room temperature of the prism and the temperature of the sample will throw off the accuracy of your reading. Remember to allow the sample to rest on the prism assembly for 30 seconds before taking a reading.

Do not expose the refractometer to damp working conditions. Do not immerse the instrument in water. If the insturment becomes foggy, water has entered the body. Call a qualified service technician or contact your dealer to purchase a new refractometer.

Do not measure abrasive or corrosive chemicals with this instrument, because they can damage the prism's coating.

Clean the instrument between each measurement using a soft, damp cloth. Failure to clean the prism on a regular basis will lead to inaccurate results and damage to the prism's coating.

The refractometer is an optical instrument. It requires careful handling and storage. Failure to do so can result in damage to the optical components and its basic structure. With care, this instrument will provide years of reliable service.

Buying Tips

When you purchase a refractometer, you'll need to know:

The range of readings (highest to lowest), to make sure it will suit your purpose. A standard range for home brewers is 0 to 32% Brix. For example, in order to achieve a 13% wine, you'll want to start your wine at a Brix of 23.

The ease with which the refractometer can be read and understood. Some less expensive refractometers are difficult to read, either due to a lack of a focus adjustment, inferior optics, or the eyepiece lacks a rubber seal and will not fit snugly over your eye.

The calibration temperature of the refractometer. The most common calibration temp is 20° C or 68° F. If your sample is not exactly 68° F, you will need to make mathematical corrections to compensate for the temperature difference. Luckily, many modern models of refractometers (like the ones stocked by grapestompers) are sold with ATC (automatic temperature compensation), so you never have to worry about the temperature of your sample.

How easy it is to calibrate. Must you purchase a calibration liquid, or can you calibrate with distilled water? Does it calibrate with a set screw or a dial or knob?

How easy it is to clean

If it comes with a protective case (they're pretty fragile) and instruction manual

Troubleshooting FAQ'S

1. There is no obvious distinction between light and dark regions.
   a. Check to make sure that you have enough sample on the measuring prism. Volatile samples may evaporate before you can take a reading.
   b. Check that the illuminating light is on and adjusted properly.
   c. If you know the approximate refractive index for your sample, depress the scale display switch on the side of the refractometer and turn the adjustment hand wheel until you are near the expected refractive index. Then release the scale display switch. If you don't see the light and dark regions try adjusting the compensator dial.
   d. If you don't know the approximate refractive index for your sample, clean the refractometer and then add a standard sample with a known refractive index. Follow the instructions for part c above. (If possible choose a standard that is similar in structure to the sample.) Then clean off the standard and add your sample.
   e. If even the scale is hard to read, adjust the focus by moving the eyepiece in and out.
2. The borderline between light and dark regions never becomes sharp, even after adjusting the compensator dial.
   a. Check to make sure that you have enough sample on the measuring prism. Volatile samples may evaporate before you can take a reading.
   b. Try readjusting the illuminating light.
3. Everything is blurry, even the scale and crosshairs.

Instrumental Chemistry

a. Adjust the focus by moving the eyepiece in and out.

4. The refractive index measured isn't correct (or at least not consistent with what is expected).
   a. Repeat the measurement, making sure that you are reading the scale correctly.
   b. Make sure you are at the same temperature as the value you are comparing to.
   c. Check the calibration of the instrument by using a sample of known refractive index. If this value also isn't correct, have the instructor or appropriate person adjust the calibration.
5. The scale doesn't show up when the switch is pressed.
   a. Make sure you are pressing the switch correctly.
   b. The light may be burned out. Consult your instructor or service technician to have it replaced.
6. The illuminating light doesn't come on.
   a. Make sure the instrument is plugged in, and that it is a live circuit.
   b. The light may be burned out. Consult your instructor or service technician to have it replaced.

Prudent Practice

Avoid Scratching the Prism

The measuring prism in many refractometers is constructed out of soft glass that is easily scratched. Be careful not to touch the glass with any hard and/or sharp object, such as a pipet tip or metal spatula. Never rub the measuring prism.

Clean the Prism Immediately After Use

Use a wetted tissue or cotton ball for cleaning the prism glass and use a dabbing motion rather than a rubbing motion to minimize the chance of scratching the prism. Good choices as cleaning solvents are ethanol or isopropanol since they are inexpensive, relatively nontoxic, and won't degrade the prism seal. If aqueous solutions are being measured, the refractometer may be cleaned with distilled water, possibly containing a small amount of nonionic detergent if necessary.

Avoid Solvents That Degrade the Prism Sealant

The sealer around the prism may be degraded by certain solvents. For example, the Bausch & Lomb Abbe' Refractometer should not be used with the following solvents:

Dimethylformamide
Dimethylacetamide
Phenols
Acetic Acid Solutions

Other solvents may degrade the sealer at slower rates and should not be used as the normal cleaning solvent:

Tetrahydrofuran
Simple Esters
Acetone

Avoid Strong Acids or Bases

Strong acids and bases will etch the prism glass.

Reporting Results

The standard format for reporting the index of refraction is shown below:

$$n_{\mathrm{D}}^{20}\ 1.3742$$

The italicized n denotes refractive index, the superscript indicates the temperature in degrees Celsius (most values are determined at 20 °C), and the subscript denotes the wavelength of light (in this case the D indicates the sodium D line at 589.3 nm). Routine refractive indexes are nearly always measured using the sodium D line, but if a different wavelength of light is used the wavelength (in nm) is inserted in place of the subscript D.

Analyzing Results and Finding Refractive Indexes

One of the most common uses of the refractive index is to compare the value you obtain with values listed in the literature. This comparison is used to help confirm the identity of the compound and/or assess its purity. The following sources list refractive indexes for a wide variety of substances:

The CRC Handbook of Chemistry and Physics
Lange's Handbook of Chemistry
The Merck Index
Chemical catalogs (e.g., the one from Aldrich Chemical Co.)
MSDS datasheets (many are available on the web)

There are also many computer-based chemical databases that contain refractive indexes. For example, both the CRC Handbook of Chemistry and Physics, and The Merck Index have computer-based versions. These can be particularly useful if your sample is an unknown and you want to search for compounds with similar indexes of refraction. One of the most comprehensive databases for organic compounds is MDL's Beilstein Crossfire database. (Last time I checked it contained 96 reported values for the index of refraction of isopropanol alone!) If you don't have access to one of the commercial chemical databases, I recommend The Organic Compounds Database at Colby College which can be used on the web for no charge.

Comparing Refractive Indexes

Since the refractive index of a substance depends on the wavelength it is important that the refractive index you are comparing to was obtained at the same wavelength as the one you determined. This is usually not an issue since the vast majority of refractive indexes are obtained using the sodium D line at 589.3 nm. (Even refractometers that use white light are normally constructed so that the refractive index obtained corresponds to that for light at 589.3 nm.)

The refractive index also depends on the temperature. Thus, it is best to obtain the refractive index of your sample at the same temperature as the value you plan to compare with; in most cases this will be 20 °C. However, if your refractometer is not equipped with a temperature regulating system, you may simply be stuck with room temperature, whatever that happens to be.

For most organic liquids the index of refraction decreases by approximately 0.00045 ± 0.0001 for every 1 °C increase in temperature. See Table 1 for a few examples. Note that the index of refraction for water is much less dependent on temperature

than most organic liquids, decreasing by about 0.0001 for every 1°C increase in temperature.

Table 1. Temperature dependence of refractive index for selected substances

Substance	n_D^{15}	n_D^{20}	n_D^{25}
Isopropanol	1.3802	1.3772	1.3749
Acetone	1.3616	1.3588	1.3560
Ethyl Acetate	1.3747	1.3742	1.3700
Water	1.3334	1.3330	1.3325

If you determined your index of refraction at a different temperature than that reported in the literature you will need to correct your value for the temperature variation before comparing it to the literature value. For example, if you determined the index of refraction of an organic liquid at 24°C, and want to compare it to a literature value determined at 20 °C, you should subtract 4(0.00045) = 0.0018 from the index of refraction you obtained.

$$\left(\begin{array}{l}\text{Refractive Index (RI)}\\ \text{at Temperature } T_1\end{array}\right) - (T_1 - T_2)(0.00045) = \text{Estimate of RI at } T_2$$

Equation for estimating the index of refraction at a temperature different than that used for the measurement. This method relies on the observation that the temperature variation in the index of refraction is similar for many organic liquids. This correction is only approximate and should not be used for aqueous solutions.

A typical laboratory refractometer can determine the refractive index of a sample to a precision of ± 0.0002. However, *small amounts of impurities can cause significant changes in the refractive index of a substance*. Thus, unless you have rigorously purified your compound, a good rule of thumb is that anything within ± 0.002 of the literature value is a satisfactory match.

Another possible source of error is miscalibration of the refractometer. This is readily checked by using a sample of known refractive index. Distilled water is a particularly convenient standard since it is nontoxic, readily available in pure form, and its refractive index varies only slightly with temperature (Table 1). If you find that the index of refraction of the standard is consistently off by more than 0.0005 from the expected value report this to your instructor or the person in charge of calibrating the refractometer.

Instrumental Chemistry

Probably the most common source of error in analog refractometers is misreading of the scale. If the index of refraction you determined seems inconsistent with other data, try repeating the measurement.

Determining Concentrations of Solutions

Determining the concentration of a solute in a solution is probably the most popular use of refractometry. For example, refractometer-based methods have been developed for determining the percentage of sugar in fruits, juices, and syrups, the percentage of alcohol in beer or wine, the salinity of water, and the concentration of antifreeze in radiator fluid. Many industries use refractometer-based methods in quality control applications. In most cases the refractive index is linearly (or nearly linearly) related to the percentage of dissolved solids in a solution (Figure 18). By comparing the value of the refractive index of a solution to that of a standard curve the concentration of solute can be determined with good accuracy. Many refractometers contain a "Brix" scale that is calibrated to give the percentage (w/w) of sucrose dissolved in water.

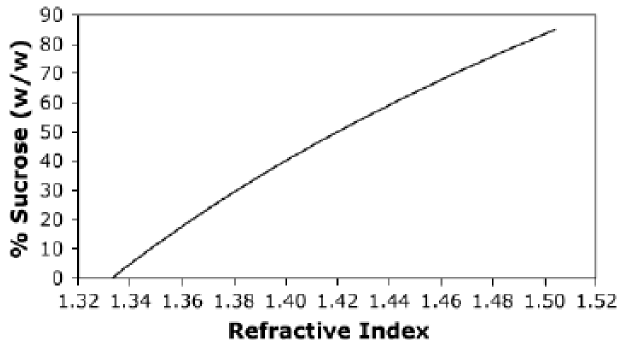


Fig. 18: A standard curve showing the relationship between the refractive index and the percentage (w/w) of sucrose in a solution of water at 20˚C.

Structural Information

The refractive index does not provide detailed information about a molecule's structure, and it is not usually used for this purpose since spectroscopic techniques are much more powerful at revealing details of molecular structure. One structural factor that influences the refractive index of a sample is its polarizability.

Instrumental Chemistry

Substances containing more polarizable ("soft") groups (e.g., iodine atoms or aromatic rings) will normally have higher refractive indexes than substances containing less polarizable ("hard") groups (e.g., oxygen atoms or alkyl groups). See Table below.

Table. Effect of polarizable groups on refractive index.

Substance	*2-Iodoethanol*	*2-Fluoroethanol*	*Benzene*	*Cyclohexane*
1.5720	1.3670	1.5010	1.4260	

Conclusion

There are many reasons why a chemist might want to use a refractometer:

To measure the percentage Brix of grapes or other fresh fruit

To determine progress of crop ripening

To measure progress of fermentation

To measure the amount of sugar present in grapes or other fruit

To allow the winemaker to determine when fruit is at its peak of ripeness and should be harvested

9

Photocolorimetery

Introduction

Most test substances in water are colorless and undetectable to the human eye. To test for their presence we must find a way to "see" them. A colorimeter or a flame spectrophotometer can be used to measure any test substance that is itself colored or can be reacted to produce a color. In fact a simple definition of colorimetry is "the measurement of color" and a colorimetric method is "any technique used to evaluate an unknown color in reference to known colors". In a colorimetric chemical test the intensity of the color from the reaction must be proportional to the concentration of the substance being tested. Some reactions have limitations or variances inherent to them that may give misleading results. Most limitations or variances are discussed with each particular test instruction. In the most basic colorimetric method the reacted test sample is visually compared to a known color standard. However, the eyesight of the analyst, inconsistencies in the light sources, and the fading of color standards limit accurate and reproducible results.

To avoid these sources of error, a colorimeter or spectrophotometer can be used to photoelectrically measure the amount of colored light absorbed by a colored sample in reference to a colorless sample (blank). A colorimeter is generally any instrument that characterizes color samples to provide an objective measure of color characteristics. In chemistry, the colorimeter is an apparatus that allows the absorbance of a solution at a particular frequency (color) of visual light to be determined. Colorimeters hence make it possible to ascertain the concentration of a known solute, since it is proportional to the absorbance.

White light is made up of many different colors or wavelengths of light. A colored sample typically absorbs only one color or one band of wavelengths from the white light. Different chemical substances absorb varying frequencies of the visible spectrum. Only a small difference would be measured between white light before it passes through a colored sample versus after it passes through a colored sample. The reason for this is that the one color absorbed by the sample is only a small portion of the total amount of light passing through the sample. However, if we could select only that one color or band of wavelengths of light to which the test sample is most sensitive, we would see a large difference between the light before it passes through the sample and after it passes through the sample. Colorimeters rely on the principle that the absorbance of a substance is proportional to its concentration i.e., a more concentrated solution gives a higher absorbance reading.

Colorimeters pass a colored light beam through an optical filter, which transmits only one particular color or band of wavelengths of light to the colorimeter's photo-detector where it is measured. The difference in the amount of monochromatic light transmitted through a colorless sample (blank) and the amount of monochromatic light transmitted through a test sample is a measurement of the amount of monochromatic light absorbed by the sample. In most colorimetric tests the amount of monochromatic light absorbed is directly proportional to the concentration of the test factor producing the color and the path length through the sample. However, for a few tests the relationship is reversed and the amount of monochromatic light absorbed is inversely proportional to the concentration of the test factor.

The choice of the correct wavelength for testing is important. It is interesting to note that the wavelength that gives the most sensitivity (lower detection limit) for a test factor is the complementary color of the test sample. For example the Nitrate-Nitrogen test produces a pink color proportional to the nitrate concentration in the sample (the greater the nitrate concentration, the darker the pink color). A wavelength in the green region should be selected to analyze this sample since a pinkish-red solution absorbs mostly green light.

Calculation

$$\text{Concentration of the Sample} = \frac{\text{Absrobance(A)of the Sample}}{\text{Absrobance (A) of the Sandard}} \times \text{Concetration of the Sandard}$$

Transmittance (T%) = log (1÷(10 $^{\text{optical density}}$) ×100

Optical Density = log (1÷(T%÷100))

Instruction for Instrument Use (See Fig 21)

Fig. 21: Showing the top view of the Photo colorimeter

Electrical Connections

The unit is complete with a three pin Mains plug suitable for a 230V 50 Hz A.C., 5A outlet. The power consumption of the unit is approximately 10 Watts.

Description

Light from a broad spectrum LED fed from a voltage stabilized solid state power supply is focused by a lens system on a photocell through a filter and test tube containing the solution. Inserting a test tube automatically removes the light shutter and allows light onto the photocell. The intensity of light can be controlled by adjusting the aperture of the lens. The output from the photocell, which is proportional to the intensity of light falling on the photocell is fed

to a solid state electronic amplifier and then measured on a Digital Display direct in Optical Density.

The LED is mounted in a funnel shaped holder and is fixed with adhesive into the holder. The holder is held by a nut on the Lens mount bracket.

The leads of the LED have a connector attached to it which goes onto the power supply card on the base of the unit.

The optical system, LED and photocell etc. are all mounted on a plate on which the controls are accessible from above.

The electrical components like the transformer, amplifier card etc. are mounted on the base plate and access to this can be had by detaching the bottom cover by removing the four screws fixing it to the housing and lifting the housing off.

Method of Use

1. Select the appropriate filter on the filter disc.
2. Place the test tube containing the solvent in the holder.
3. Adjust the sensitivity control for 0.00 0.0. reading on the display. Rotating the control away from you increases the intensity of light.
4. Replace test tube containing solvent with one containing the solution. and take the reading.
5. The display is in Optical Density and ideally should be used for estimations in the range of 0.2 to 0.6 Density. There may be variations in the test tube up to about 1 % Transmission. This is inherent in the nature of the test tubes. It is to minimize the effect of this variation, that the preferred range of 0.2 to 0.6 Densities has been indicated. When the shutter is closed (no test tube), the display will show “1» only. This is an over range indication and equivalent to 0% Transmission. A table showing the relation of Transmission and Optical Density at salient points of the scale is in this manual.
6. One ml. of solution is adequate to cover the light path of the test tubes. Please take care not to grossly overfill the test tubes.

Filters

In the eight filter version, narrow band filters are used in place of glass filters with peak transmission at 700, 610, 580, 550, 520, 490, 470 and 430 millimicrons.

The tables below shows the different absorption transmittance at the application of different filters.

% transmittance vs Absorbance

%T	A	%T	A
0	—	50	0.3010
5	1.3010	60	0.2218
10	1.0000	70	0.1549
20	0.6990	80	0.0969
30	0.5229	90	0.0458
40	0.3979	100	0.0000

Filter	Colour	Pass Band
700	Red	6200°A - Infra Red
610	Orange	5750°A - Infra Red with Peak at 6000°A
580	Yellow	5600°A - 6100°A
550	Yellow Green	5300°A - 5700°A
520	Green	5000°A - 5400°A
490	Blue Green	4700°A - 5200°A
470	Blue	4400°A - 4900°A
430	Violet	3800°A - 4700°A

Maintenance

Apart from normal cleaning and care this instrument requires little or no maintenance as such.

Using Photocolorimeter as a Visual Spectrophotometer

A photo colorimeter can be also used a visual spectrophotometer, by a simple process of taking the reading of absorbance of a solution at all the 8 wavelengths of light and calculating the transmittance by the application of the formulae stated above. The curves below show the spectrum of the specimen solutions.

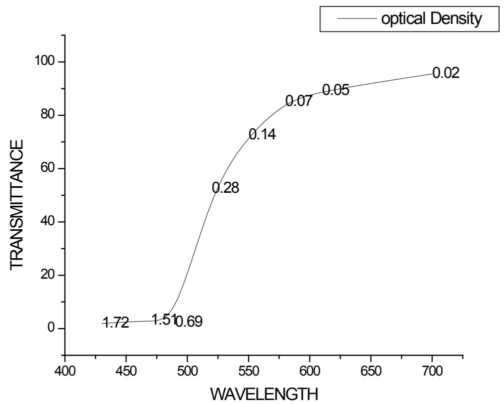


Fig. 22A: Showing the curve of the transmittance (T%) against the wavelength and absorbance (OD) of chromic anhydride.

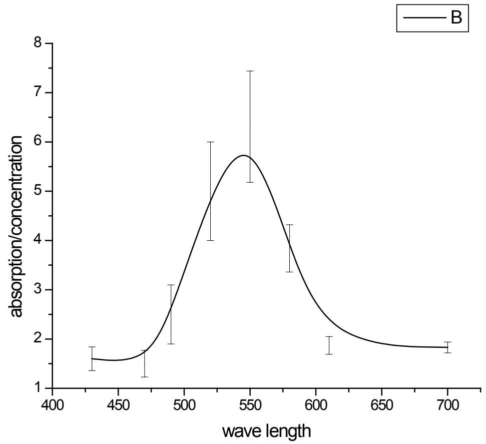


Fig. 22B: Showing the Absorbance- concentration against the wavelength of .01m/L KMnO4 solution

10

Flame Spectrophotometer

History

In 1860 Robert Bunsen (1811–1899) and Gustav Kirchhoff (1824–1887) discovered two alkali metals, cesium and rubidium, with the aid of the spectroscope they had invented the year before. These discoveries inaugurated a new era in the means used to find new elements. The first 50 elements discovered—beyond those known since ancient times—were either the products of chemical reactions or were released by electrolysis. From 1860 the search was on for trace elements detectable only with the help of specialized instruments like the spectroscope.

Bunsen, the son of a professor of modern languages at Göttingen University in Germany, earned his doctorate from that university in 1830. He was then given a three-year travel grant that took him to factories, places of geologic interest, and famous laboratories, including *Joseph Louis Gay-Lussac's* in Paris. Early in his career he did research in organic chemistry, which cost him the use of his right eye when an arsenic compound, cacodyl cyanide, exploded. Throughout his career he remained deeply interested in geological topics and once made daring temperature measurements of the water in the geyser tube of Iceland's Great Geyser just before it erupted.

Bunsen and Kirchhoff, a Prussian physicist trained at Königsberg, met and became friends in 1851, when Bunsen spent a year at the University of Breslau, where Kirchhoff was also teaching. Bunsen was called to the University of Heidelberg in 1852, and he soon arranged for Kirchhoff to teach at Heidelberg as well.

Bunsen's most important work was in developing several techniques used in separating, identifying, and measuring various chemical substances. He also made a number of improvements in chemical batteries for use in isolating quantities of pure metals—including one known as the Bunsen battery. He created the Bunsen burner for use in flame tests of various metals and salts: its nonluminous flame did not interfere with the colored flame given off by the test material.

This line of work led to the spectroscope. It was Kirchhoff who suggested that similarly colored flames could possibly be differentiated by looking at their emission spectra through a prism. When he shone bright light through such flames, the dark lines in the absorption spectrum of the light corresponded in wavelengths, with the wavelengths of the bright, sharp lines characteristic of the emission spectra of the same test materials.

Bunsen spent the last 40 years of his career at Heidelberg. Young chemists flocked to him, including Julius Lothar Meyer and Dmitri Mendeleev.

As a direct result of the work done by Kirchoff and Bunsen in the early 1860's, the possibility of using the characteristic radiation emitted by atoms excited in flames for quantitative analysis was realised.

Soon after, an instrument was developed for the quantitative analysis of Sodium in plant ash using a Bunsen flame

The major problems experienced over the next 60 years were that of finding a reproducible method of introducing a sample into a flame and to then find a convenient technique to measure the emission of intensity.

Lundegardh largely overcame these difficulties in the 1920's whose apparatus included a nebuliser that enabled the sample to be presented to the air/acetylene flame in aerosol form. The emission was dispersed by a quartz prism spectrograph and recorded photographically. Precision was typically 5 – 10%

Greater convenience resulted from the introduction of simple coloured filters for wavelength selection, together with photocell/galvanometer combinations for measuring intensities directly. As

a result simple and inexpensive instruments of this type using air/coal gas or air/acetylene flames became widely available from the late 1940's for the determination of Sodium, Potassium, Lithium and Calcium.

Work on many other elements then became possible with the use of grating spectrometers equipped with photo multiplier detectors through to the development of atomic absorption in the late 1960's, which restricted the use of flame emission.

However, there is a widespread requirement for the estimation of the alkali metals and for this purpose low temperature flame photometry provides the most reliable and convenient procedure available.

Principles of Flame Spectrophotometry

The basis of flame spectrophotometry is the same as that of the simple quantitative analytical flame test. This exploits the fact that compounds of the alkali and alkaline earth metals are thermally dissociated into atoms at the temperature of a Bunsen burner flame and that some of the atoms produced are further excited to a higher energy level. When these 'excited' atoms return to the ground state, they emit radiation, which for the elements of these two groups lies mainly in the visible region of the electromagnetic spectrum

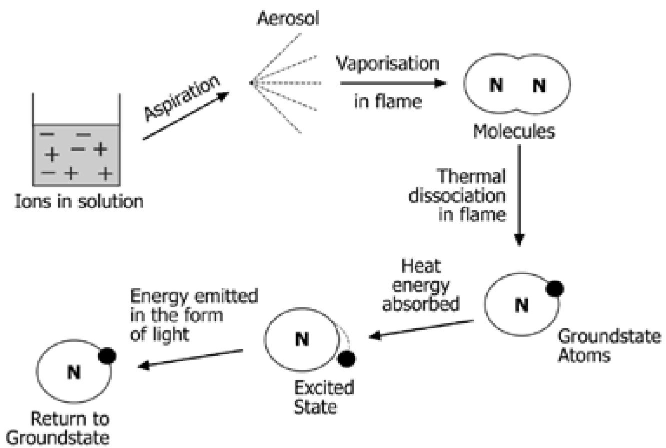


Fig. 23: Showing the Theoretical Diagram of Flame Spectrophotometry

The wavelength of the light emitted from the flame is characteristic of the particular element.

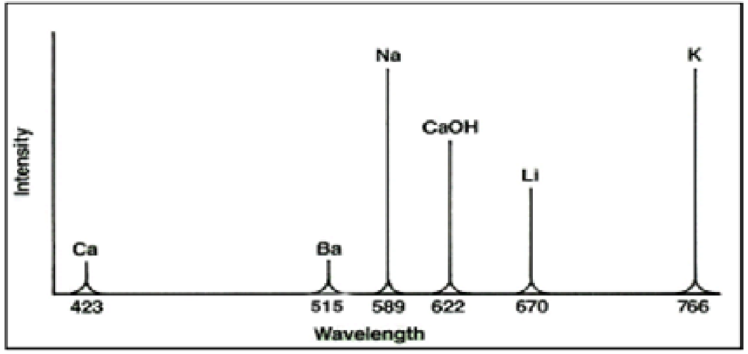


Fig. 24: Intensities of emissions of the elements at equal concentrations and their wavelengths

The intensity of this light is, in most cases, proportional to the absolute quantity of the species present in the flame at any moment. The number of atoms returning to the ground state is proportional to the number of atoms excited, i.e. the concentration of the sample.

This relationship applies only at low concentrations

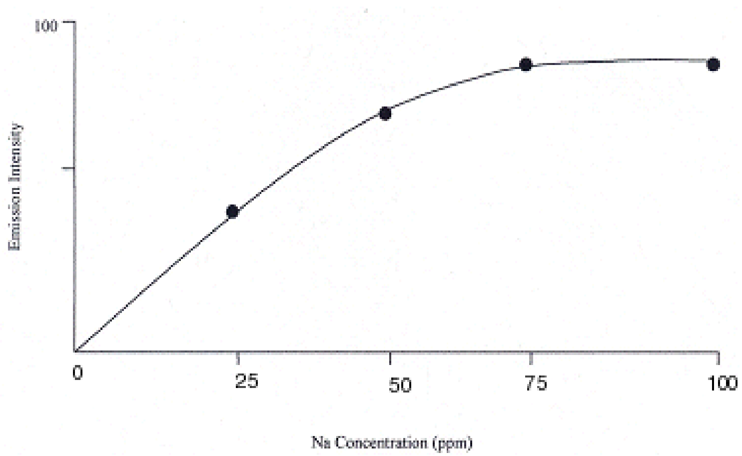


Fig. 25: Showing the curve of the Concentration of Sodium in a sample

The emitted radiation is isolated by an optical filter and then converted to an electrical signal by the photo detector.

Principles of Operation

Flame Spectrophotometry relies upon the fact that the compounds of the alkali and alkaline earth metals can be thermally dissociated in a flame and that some of the atoms produced will be further excited to a higher energy level. When these atoms return to the ground state they emit radiation which lies mainly in the visible region of the spectrum. Each element will emit radiation at a wavelength specific for that element. The table below gives details of the measurable atomic flame emissions of the alkali and alkaline earth metals in terms of the emission wavelength and the colour produced.

Element	Emission Wavelength (nm)	Flame Colour
Sodium (Na)	589	Yellow
Potassium (K)	766	Violet
Barium (Ba)	554	Lime Green
Calcium (Ca)	622*	Orange
Lithium (Li)	670	Red

**Note*: Calcium is measured by using the calcium hydroxide band emission at 622 nm as the Calcium main atomic emission occurs at 423 nm.

Over certain ranges of concentration the intensity of the emission is directly proportional to the number of atoms returning to the ground state. This is in turn proportional to the absolute quantity of the species volatized in the flame, i.e. light emitted is proportional to sample concentration. It can be seen that if the light emitted by the element at the characteristic wavelength is isolated by an optical filter and the intensity of that light measured by a photo-detector, then an electrical signal can be obtained proportional to sample concentration. Such an electrical signal can be processed and the readout obtained in an analogue or digital form.

A simple flame spectrophotometer consists of the following basic components:

a. *The burner*: a flame that can be maintained in a constant form and at a constant temperature.
b. *Atomizer and mixing chamber*: a means of transporting a homogeneous solution into the flame at a steady rate.

Instrumental Chemistry

c. *Simple colour filters (interference type)*: a means of isolating light of the wavelength to be measured from that of extraneous emissions.

d. Atomic Absorption filters are also associated to the instrument to extract the element from the sample and standard solutions

e. Photo-detector: a means of measuring the intensity of radiation emitted by the flame.

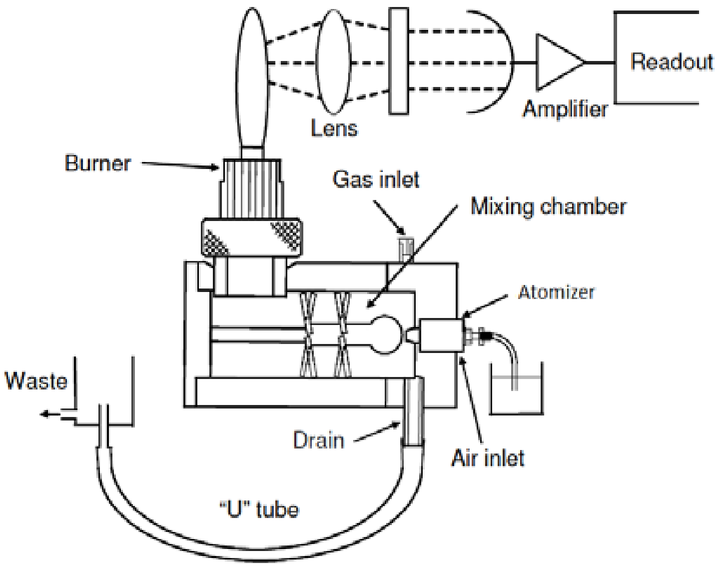


Fig. 26: Basic components of a Flame Spectrophotometer

The analysis of alkali and alkaline earth metals by flame photometry has two major advantages:

i. Their atoms reach the excited state at a temperature lower than that at which most other elements are excited.

ii. Their characteristic wavelengths are easily isolated from those of most other elements due to wide spectral separation.

The analysis of Na, K, Li, Ba and Ca are typically determined at low temperatures, i.e. 1500-2000°C, therefore suitable fuel mixtures are propane/air, butane/air and natural gas/air (but it is suggested that natural gas or LPG must be used other combinations can be

harmful and misleading.

Specification

Ranges: - 120-160 mmol/l Na (linearised)

0-10.0 mmol/l K

Limits of Detection

Na	≤ 0.2ppm		-
K	≤ 0.2ppm		-
Li	≤ 0.25ppm	Li	≤ 0.25ppm
Ca	≤ 15ppm	Ca	≤ 15ppm
Ba	≤ 30ppm	Ba	≤ 30ppm

Reproducibility: 1% Coefficient of variation (C.V.) for 20 consecutive samples using 10ppm Na set to read 50.0.Readings taken at 20 second intervals.

N.B. C.V. is defined as: the sample standard deviation X 100

mean reading

And sample standard deviation as:

$$\sqrt{\frac{\overline{X}-X^{2}}{n-1}}$$

Where the reading, x is the mean readings of the series and n is the number of readings.

Linearity: Better than 2% when concentration of 3ppm Na and K and 5ppm Li are set to read 100.

Specificity: Interference from Na, K and Li when equal in concentration to the test element will be less than 0.5%.

Stability: Better than 2% over 5 minutes when continuously aspirating 10ppm, sample set to read 50.0. Zero drift better than 2% per hour.

Sample Requirements: Between 2 and 6ml/minute.

Recorder Output: Nominal 1.00 volt for readout of 100.0.

Warm Up: The flame must be alight for at least 15 minutes to ensure achievement of the above stated specifications.

Services: Electrical: 90-125V or 190-250V @ 50/60Hz.

Air: Moisture and oil-free 6 litres/minute at 1kg/cm2 (14psi).

Fuel: natural gas or L.P.G.

Operating Environment: 15°C to 35°C

Instructions for Use of Fotoflame Spectrophotometer

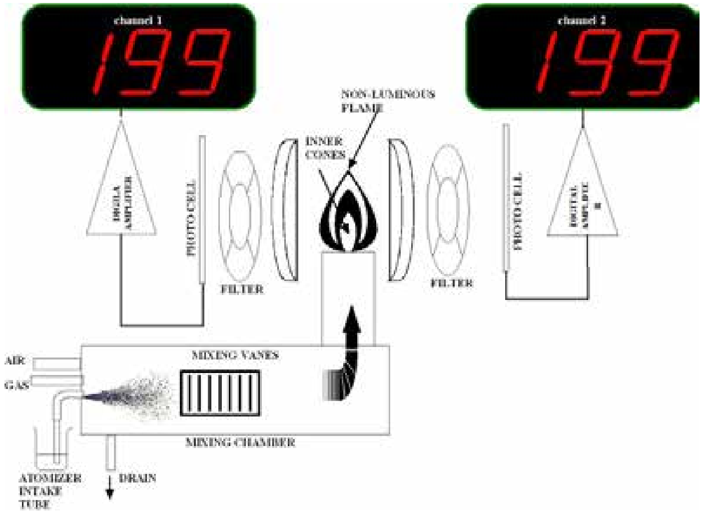


Fig 27: Showing the Schematic Diagram of the Aimil Photo flame Flame Spectrophotometer

Fig. 27A & 27B: Showing the Front Panel and the back side of the Flame Spectrophotometer and its compressor

General Description

The FOTOFLAME FLAME SPECTROPHOTOMETER is suitable for estimation of alkali metals and alkali earth metals. The equipment is normally supplied with filters for determination of Sodium and Potassium. It works on the principle that when a solution of the metallic salt is sprayed into a non-luminous flame, the flame emits light of a characteristic wavelength. The intensity of this emission is proportional to the concentration of the metal in the solution.

Fig. 27C: The Atomizer intake of the Flame Spectrophotometer

The general layout of the instrument is shown if Fig. (27), Gas and air are introduced at a controlled rate into the mixing chamber (3). The air, while flowing into the chamber, draws in the liquid (1) through the capillary (fig 27c) and atomizes it into a fine spray. The mixture of gas, air and atomized liquid is ignited at the burner top (5). The excess liquid which has not atomized properly is drained off from the mixing chamber. The light emitted from the flame passes through the lens (9) and filter (10) and then falls on the photocell (11). The filter transmits only the wavelength characteristic of the element being estimated. The output from the photocell is fed to the amplifier (12) and the amplified signal is measured on a Digital Display reading up to 199.

In the DUAL CHANNEL version of the instrument, there is another set of Lenses, Filter and Detector as marked (9A, 10A & 11 A). A separate amplifier (12A, fig. 27) and Display (13A, .Fig. 27) is used for this channel. Normally, the 'K' (Potassium) filter is fixed in this channel whereas the four position filter disc (10, fig. 27) holds the Na and other filters. Both displays in this unit are Digital (0 to 199) and have separate Zero & Sensitivity controls.

The approximate concentrations required for obtaining 100 0n displays are as follows:

Sodium	4 ppm
Potassium	2 ppm

Higher concentrations can also be estimated, but it is not advisable to use very concentrated solutions as this saturates the flame and gives non-linear results. It is preferable to draw a calibration curve for one particular range of concentrations and the solution to be estimated should be diluted to fall within this range.

The atomizer takes up liquid approximately at the tare of 5 ml. per minute, and as it is possible to take a reading in about 20 seconds, only 1 or 2 ml. of the sample is consumed.

Main Features

1. **Electrical Ignition**: An electrical system is provided. Pushing in the knob (3, Fig. 2) switches on the current to the ignition filament and at the same time brings it, into position over the burner top. When the flame ignites and the knob is released, the filament current is automatically switched off and the filament also springs back away from the flame.
2. **Viewing Window**: A viewing window (11, Fig. 27) is provided at eye-level to the seated operator of the instrument. This window enables the operator:
   (a) to see the operation of the ignition filament.
   (b) to watch the flame when making the necessary gas and air adjustments.
   (c) to watch the colour changes in the flame when the test solution is being fed through the atomizer intake-this last giving an immediate indication of clogging of the intake capillary which may occur from time to time.
3. **Sensitivity Control**: The sensitivity control (4, Fig. 27) is the gain control of the amplifier which gives a fine control of sensitivity, and a High/Low switch is provided on the main panel, the two enabling accurate setting of 100.
4. **Stabilised Amplification**: The solid state amplifier uses IC only. The D.C. supply to the amplifier is also regulated by IC This is a special low level amplifier which is designed to ensure linear amplification of the Photocell response.
5. **Rotating Filter Mount**: The filters for use with Sodium and Potassium respectively are mounted on a rotating disc within the unit itself safe from dust, scratches and misplacement or loss. The knurled edge of the disc (2, Fig. 27) showing through the cover enables it to be turned to the required setting when the symbol corresponding to the element being estimated shows on top and an internal spring catch engages and holds the disc in position. A maximum of four filters can be accommodated in the disc.

Setting Up

(1) Connect a tube to the drain outlet nipple on the bottom back right side of the unit. This tube should be long enough to reach the disposal point and should be progressively sloping downwards. Four cups are provided for use under the feet of the instrument, to raise the unit and provide adequate slope to drain excess liquid. These may be used if necessary. To prevent liquid buildup in the chamber, the drain is provided with overflow holes. If there is inadequate drainage, water will overflow and collect under the unit. If there is continuous overflow of water from the drain channel, place a Petri dish under the drain outlet to collect the overflow. Empty this periodically.

In the DUAL CHANNEL unit, K filter is fixed into the second channel. The Na and other filters (where ordered) are fitted on the Filter Disc.

***Warning**: The gas and air inlets are marked clearly. The Connections must be made correctly and checked before turning on the air supply. Otherwise the instrument will be damaged. Explosions can occur.*

The instrument works on bottled gas (LPG krebson) etc.) as well as on laboratory gas supply, the pressure of which should not be less than 12 cm. of water-gauge. Acetylene or compressed Oxygen should never be used on this instrument as both will cause explosion and damage.

(2) Place the chimney top (1, Fig. 27) in the recess on the top.

(3) Connect the nipples at the back of the unit to the gas and compressed air supply by suitable lengths of rubber tubes.

Instrumental Chemistry

(4) Remove the plastic shield (6, Fig. 2) (2 thumb nuts on the right of the instrument) used in transit and replace thumb nuts on cover plate.

(5) Connect the 3-pin plug to the mains 230V. A.C., 50Hz., single phase. Ensure proper earthing is available.

(6) Connect the Compressor to the mains.

(7) Fit the atomizer intake P. V. C. tube to the atomizer, sliding it on to the tip of the atomizer needle.

Operation

(1) Switch on the mains using the switch provided at the back of the instrument.

(2) Set the appropriate filter in position by rotating the filter drum till the spring loaded catch engages the disc with the appropriate symbol (K-¬potassium, Na-Sodium or Ca-Calcium) showing on top.

(3) Put a beaker containing distilled water under the atomizer intake tube and raise it till the tube dips into the water.

(4) Turn on the compressed air supply by starting the compressor.

(5) Adjust the air pressure to about 2 P.S.I. (0.125 Kg.lsq. em.) by means of the air control valve (8, Fig. 27) (turning it clockwise reduces the air supply).

(6) Close the gas valve by turning it clockwise until the end stop is reached. Now turn it one turn anti-clockwise.

(7) Push the ignition knob (3, Fig. 27) in. This brings the filament in position for ignition as well as switches on the mains to the primary of the low voltage transformer which supplies the heating current to the filament. The filament will be seen glowing near the edge of the burner when seen from window (11, Fig. 27).

(8) Now turn on the gas supply. The flame should now ignite. This can be observed through the viewing window (11, Fig. 27). If it does not ignite, open the gas control valve (9, Fig. 2) by turning it anti-clockwise till the flame ignites.

The electrical ignition system will not work if the mains voltage is low as the filament will not reach to the ignition temperature. In such a case the flame could be ignited by introducing a lighted taper inside the chamber through the chimney. It may take 10-15 seconds for the gas to reach the burner top and ignite. If it does not ignite in this time, turn off the gas mains, wait a few minutes to allow the collected gas to dissipate. Try once again by manual ignition with a lighted taper.

Do not put the gas supply on before the filament is seen glowing hot or lighted taper is introduced into the chamber as this may result in collection of gas inside the instrument and cause explosion.

(9) Adjust the air pressure to about 10 p.s.i (see red mark on the dial) (0.7 Kg./sq. cm.) and then adjust the gas flow by operating gas control valve (9, Fig. 27) to obtain a NON LUMINIOUS BLUE FLAME WITH WELL DEFINED GREENISH BLUE INNER CONES SETTLED ON THE GRID HOLES ON THE BURNER TOP(see fig 27E1). Such a flame is stable and suitable for measurements. With a rich mixture Le. increased gas supply; the inner cones will elongate and merge into each other making the flame luminous, while with lean mixture Le., decreased gas supply, these cones will change to bluish violet, the flame will become unstable

Fig. 27D: Showing the Burner and the filter from the top. (Left)

Instrumental Chemistry

Fig. 27E1: Showing the Non-luminous flame (middle)

Fig. 27E2: Showing the flame after the absorption of the standard (right)

and noisy before lifting up from the burner top and blowing off. While making these adjustments the flame should be watched from the observation window and the gas and air controls should be operated slowly and gradually.

In case flame blows off, shut the gas supply from the source, reduce the air pressure to about 2 p.s.i and follow the ignition procedure given in (7) and (8). If the air pressure is not reduced to 2 p.s.i the filament may not reach the ignition temperature because of the cooling caused by the strong draft of air.

(10) Wait for 5 minutes for the flame to stabilize and then replace the distilled water by a reagent "blank".

(11) Adjust the Display reading to zero (with sensitivity control turned clockwise) by means of the zero control knob (5, Fig. 27)

(12) Replace the reagent "blank" by a "standard" solution with highest concentration in the range of estimation and adjust the sensitivity control (4, Fig. 27) to get 100 on Display.

(13) Feed the reagent "blank" and re-adjust zero if necessary.

(14) Feed the "standard" and again adjust the reading to 100, if necessary by using the sensitivity control.

(15) Recheck the zero reading once again with "blank".

(16) Feed the sample solution and take the reading on the Display.

To use both channels simultaneously in the DUAL CHANNEL unit, repeat steps 10 to 15 with the second channel as well. It is preferable to flush the system with distilled water or reagent "blank" between each sample, especially after estimating a concentrated sample. It is not necessary to flush the system if samples of nearly similar concentration are being examined in quick succession.

Operation Precautions

1. The fuel gases used in the flame photometers are inflammable and therefore potentiallyhazardous. Cylinders of fuel gas should always be stored and used in line with the supplier's recommendation.
2. It is possible that a small quantity of fuel will escape from the instrument during the ignition sequence. The amount of fuel is harmless although may smell slightly. If the smell of fuel gas persists the instrument should be immediately shut down and the source of the leakage determined by using a soap solution on the hose joints.
3. Do not leave the instrument running unattended while the flame is alight.
4. The top of the instrument chimney unit becomes very hot when running and can cause severe burns if touched.
5. The exhaust gases from the flame are very hot and the area approximately 1 metre above the chimney must be avoided. Never attempt to look down the chimney whilst the flame is running. Always use the inspection window.
6. The instrument uses potentially hazardous electrical supplies. Never remove covers from the instrument without first ensuring that it has been isolated completely from the AC mains supply
7. If the instrument is used in a pathology laboratory, all samples should be handled with the caution normally accorded to those known to contain pathogenic organisms. Care should also be taken when undertaking maintenance on instruments that have been used in these environments. A bactericidal agent should be used when cleaning parts

Instrumental Chemistry

during routine maintenance.

Good practice guidelines

1. It is most important that the nebuliser, mixing chamber and burner are kept clean by carrying out the correct shutdown procedure and by periodic maintenance. If high salt solutions are aspirated, correspondingly longer periods should be spent aspirating deionised water prior to shutdown.
2. It is recommended that blank and standard solutions should have a wetting agent (e.g. EMARK DEIONIZED WATER OR DEIONIZED WATER PREAPRED IN LAB added to promote good stability and self cleaning. Any such wetting agent should be non-ionic and used at a concentration of 0ppm. It should be added to the blank, standards and samples at the same concentration.
3. Take care when preparing standards. The performance of the instrument depends upon the accuracy and purity of the calibration standards.
4. If standard solutions are required to be stored for any length of time or at an elevated temperature, a suitable mould inhibitor e.g. azide should be added. However if this contains the element to be measured (e.g. sodium) it is important that the samples also contain an equivalent amount.
5. Always sample from the top half of the sample container. The bottom half may contain sediment or particulate matter which could easily block the fine tubing used in the atomizer
6. Always use recommended spares. Even where an alternative part may be obviously suitable there may be good reasons for not using it.
7. Never use glass containers to store calibration standards.

Calibration

The output from the photocell measured as the reading on Display is linear with reference to the intensity of emission. But the relation between the concentration of the solution and the intensity

of emission may not necessarily be linear. It is, therefore, necessary to draw a calibration curve by using solutions of known concentrations for a particular range. The samples to be estimated should lie within this range.

A 4 ppm sodium chloride solution is applied after the instrument has aspired a 2 ml of distilled water the display is adjusted to 100 and again the distilled water is aspired to read the display as 000 the instrument is calibrated

It is important to understand that the principles of flame photometry are such that, over certain concentration ranges, light emitted from the flame is directly proportional to the concentration of the species being aspirated. The graph below shows that the direct relationship between the flame emission and concentration is only true at relatively low concentrations. Above these low levels the flame begins to saturate and the flame emission ceases to increase in a linear relationship to concentration.

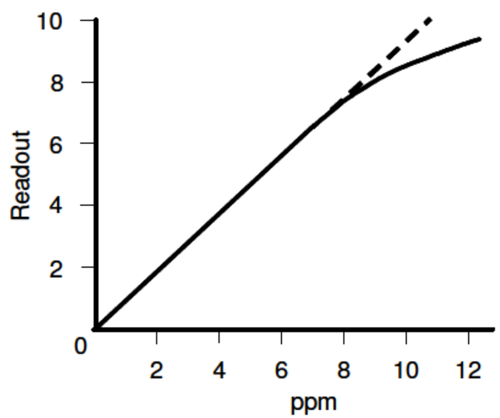


Fig. 28: Relationship between sample concentration and flame emission.

If the samples being analysed lie on the linear part of the curve then the user can take direct concentration readings from the digital display. If, however, the concentration of samples are above the levels shown on the graph then the user has the choice of either:

a. diluting the samples so that they lie on the linear part of the curve, or

b. constructing a calibration curve and relating the digital display reading to the concentration by cross-reference to the curve.

A calibration curve is prepared using standard solutions containing known concentrations of the elements to be determined and if necessary, other materials to ensure that the standard and sample backgrounds match. The concentration range covered by the calibration curve will depend upon the expected concentration of the samples so that the sample readings fall somewhere in the middle of the calibration curve. Once the calibration curve has been plotted, the readings for the sample solutions are compared with the curve to allow the sample concentrations to be established. It is important to realize that each element has its own characteristic curve and separate calibration curves must be constructed.

If the same estimation is performed on a routine basis, the calibration curve need only be prepared once and checked periodically. Instrument re-calibration is easily achieved by setting the blank solution to read zero and the top standard to read the same value as it did when the calibration curve was initially prepared. The graph in Figure 29 shows a typical curve obtained when measuring in parts per million (ppm).

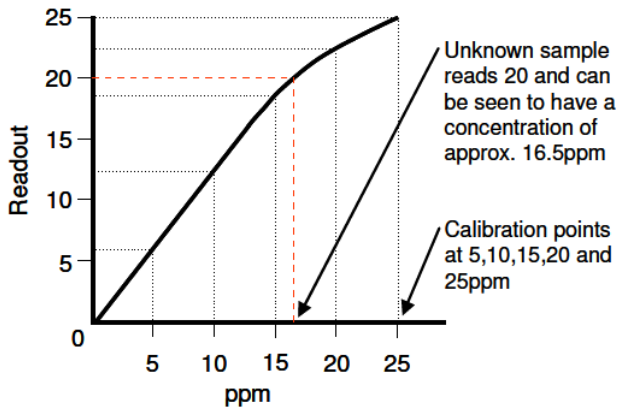


Fig. 29: Typical calibration curve measuring ppm

The peoples working in medical environments are quite likely to be using the S.I. unit of mmol/l to report their results. The ppm to

mmol/l can be obtained by a simple calculation formula:

$$\text{mmol} = \frac{\text{ppm}}{\text{atomic weight}}$$

The relationship between mmol/l and ppm is defined below:

Sodium Na 1ppm = 0.0435mmol/l 1mmol/l = 23ppm

Potassium K 1ppm = 0.0256mmol/l 1mmol/l = 39ppm

Lithium Li 1ppm = 0.1441mmol/l 1mmol/l = 7ppm

Calcium Ca 1ppm = 0.0250mmol/l 1mmol/l = 40ppm

This relationship means that Na and K samples in the normal clinical range of 136-145mmol/l

Na and 3.5-5.0mmol/l K should be pre-diluted 1 in 100 or 1 in 200 to get optimum results from the flame spectro-photometer.

1. Aspirate a blank solution and set the readout to 000 using the blank control.
2. Aspirate the highest standard solution and set the readout to an appropriate reading using the sensitivity controls. Re-check the blank setting and adjust if necessary.
3. Aspirate the remaining standard solutions (if used) to construct the calibration curve and note the results.
4. When the blank and standards are set, unknown samples can be aspirated and the results noted, either directly from the instrument readout, or by deriving the concentrations from the calibration curve.
5. Calibration needs to be checked periodically by aspirating the blank and standard solutions. Initially this check should be carried out after every 10 samples. Experience and increased confidence in the PFP7 will enable you to best judge the frequency of this check.
6. The decimal point (d.p.) switch can be set to illuminate the decimal point in any significant position. This should be chosen to give sufficient resolution for the test required.

Switching Off

Before switching off, flush the system clean with distilled water. In routine course, the air and gas controls should

This is very important do not make it reverse

be left undisturbed and the air and gas should be turned off at the source.

Follow the sequence below in turning off gas and air.

(1) Turn off the gas, the flame will extinguish.
(2) Turn off the air.
(3) Switch off the mains.

Maintenance and Servicing

The most important aspect of maintenance is to keep the atomizer, mixing chamber, burner and optical assembly clean for reliable and accurate results. Apart from this, very little attention is required except when there is a component failure. The appropriate procedures for this work are given below:

Cleaning atomizer needle and intake capillary: Normally flushing with distilled water and introducing the cleaning wire is all that is required to remove any solid particles which might be present in the solution. In case these fail to clear the blocked orifice, proceed as follows:

The Atomizer is a straight plug with two '0' rings for sealing and a screw cap to hold it in place. No force needs to be used to insert or remove the Atomizer. Once the screw cap is unscrewed, the atomizer plug can be removed by gentle handling. The Atomizer itself is made of a special epoxy resin. For cleaning the Atomizer, either detergent solution, or an organic solvent like Xylene may be used. Do not use mechanical means to clean the atomizer since this may lead to an increase or change in the small air holes which are of critical dimensions.

Preparation for Analysis

Calibration standards

A comprehensive range of aqueous calibration standards is available from Emark in both industrial and clinical levels. These must be diluted to a suitable concentration for aspiration into the flame

Clinical Standards (500ml)

1.00mmol/l Li

10

Flame Spectrophotometer

History

In 1860 Robert Bunsen (1811–1899) and Gustav Kirchhoff (1824–1887) discovered two alkali metals, cesium and rubidium, with the aid of the spectroscope they had invented the year before. These discoveries inaugurated a new era in the means used to find new elements. The first 50 elements discovered—beyond those known since ancient times—were either the products of chemical reactions or were released by electrolysis. From 1860 the search was on for trace elements detectable only with the help of specialized instruments like the spectroscope.

Bunsen, the son of a professor of modern languages at Göttingen University in Germany, earned his doctorate from that university in 1830. He was then given a three-year travel grant that took him to factories, places of geologic interest, and famous laboratories, including *Joseph Louis Gay-Lussac's* in Paris. Early in his career he did research in organic chemistry, which cost him the use of his right eye when an arsenic compound, cacodyl cyanide, exploded. Throughout his career he remained deeply interested in geological topics and once made daring temperature measurements of the water in the geyser tube of Iceland's Great Geyser just before it erupted.

Bunsen and Kirchhoff, a Prussian physicist trained at Königsberg, met and became friends in 1851, when Bunsen spent a year at the University of Breslau, where Kirchhoff was also teaching. Bunsen was called to the University of Heidelberg in 1852, and he soon arranged for Kirchhoff to teach at Heidelberg as well.

Bunsen's most important work was in developing several techniques used in separating, identifying, and measuring various chemical substances. He also made a number of improvements in chemical batteries for use in isolating quantities of pure metals—including one known as the Bunsen battery. He created the Bunsen burner for use in flame tests of various metals and salts: its nonluminous flame did not interfere with the colored flame given off by the test material.

This line of work led to the spectroscope. It was Kirchhoff who suggested that similarly colored flames could possibly be differentiated by looking at their emission spectra through a prism. When he shone bright light through such flames, the dark lines in the absorption spectrum of the light corresponded in wavelengths, with the wavelengths of the bright, sharp lines characteristic of the emission spectra of the same test materials.

Bunsen spent the last 40 years of his career at Heidelberg. Young chemists flocked to him, including Julius Lothar Meyer and Dmitri Mendeleev.

As a direct result of the work done by Kirchoff and Bunsen in the early 1860's, the possibility of using the characteristic radiation emitted by atoms excited in flames for quantitative analysis was realised.

Soon after, an instrument was developed for the quantitative analysis of Sodium in plant ash using a Bunsen flame

The major problems experienced over the next 60 years were that of finding a reproducible method of introducing a sample into a flame and to then find a convenient technique to measure the emission of intensity.

Lundegardh largely overcame these difficulties in the 1920's whose apparatus included a nebuliser that enabled the sample to be presented to the air/acetylene flame in aerosol form. The emission was dispersed by a quartz prism spectrograph and recorded photographically. Precision was typically 5 – 10%

Greater convenience resulted from the introduction of simple coloured filters for wavelength selection, together with photocell/galvanometer combinations for measuring intensities directly. As

a result simple and inexpensive instruments of this type using air/coal gas or air/acetylene flames became widely available from the late 1940's for the determination of Sodium, Potassium, Lithium and Calcium.

Work on many other elements then became possible with the use of grating spectrometers equipped with photo multiplier detectors through to the development of atomic absorption in the late 1960's, which restricted the use of flame emission.

However, there is a widespread requirement for the estimation of the alkali metals and for this purpose low temperature flame photometry provides the most reliable and convenient procedure available.

Principles of Flame Spectrophotometry

The basis of flame spectrophotometry is the same as that of the simple quantitative analytical flame test. This exploits the fact that compounds of the alkali and alkaline earth metals are thermally dissociated into atoms at the temperature of a Bunsen burner flame and that some of the atoms produced are further excited to a higher energy level. When these 'excited' atoms return to the ground state, they emit radiation, which for the elements of these two groups lies mainly in the visible region of the electromagnetic spectrum

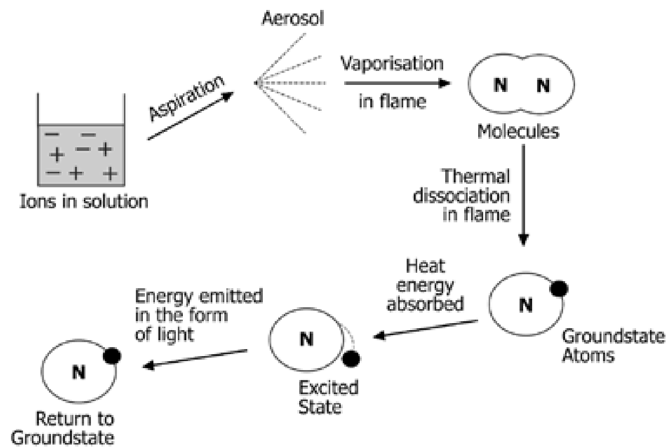


Fig. 23: Showing the Theoretical Diagram of Flame Spectrophotometry

The wavelength of the light emitted from the flame is characteristic of the particular element.

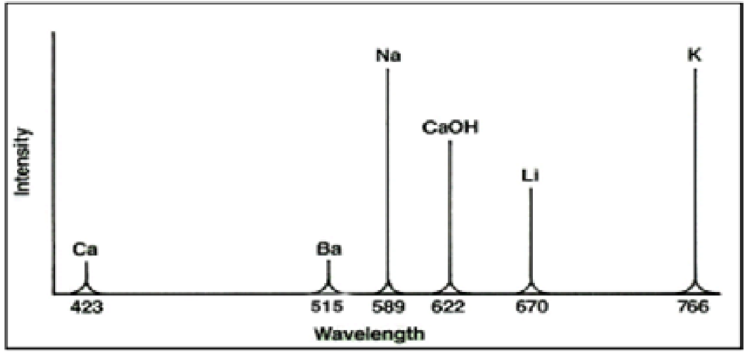


Fig. 24: Intensities of emissions of the elements at equal concentrations and their wavelengths

The intensity of this light is, in most cases, proportional to the absolute quantity of the species present in the flame at any moment. The number of atoms returning to the ground state is proportional to the number of atoms excited, i.e. the concentration of the sample.

This relationship applies only at low concentrations

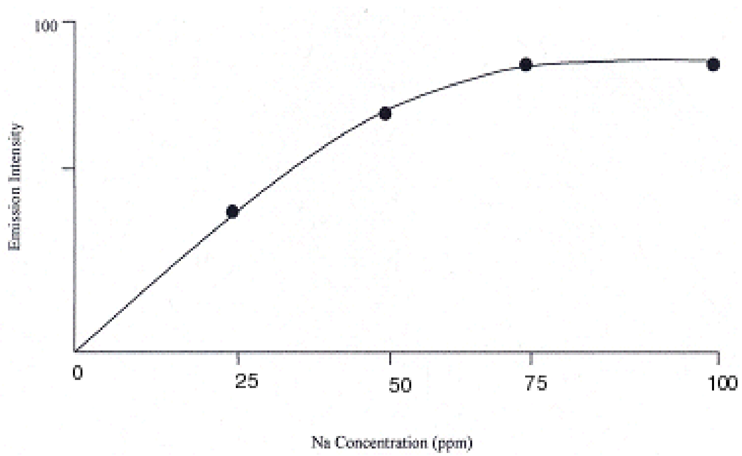


Fig. 25: Showing the curve of the Concentration of Sodium in a sample

The emitted radiation is isolated by an optical filter and then converted to an electrical signal by the photo detector.

Principles of Operation

Flame Spectrophotometry relies upon the fact that the compounds of the alkali and alkaline earth metals can be thermally dissociated in a flame and that some of the atoms produced will be further excited to a higher energy level. When these atoms return to the ground state they emit radiation which lies mainly in the visible region of the spectrum. Each element will emit radiation at a wavelength specific for that element. The table below gives details of the measurable atomic flame emissions of the alkali and alkaline earth metals in terms of the emission wavelength and the colour produced.

Element	Emission Wavelength (nm)	Flame Colour
Sodium (Na)	589	Yellow
Potassium (K)	766	Violet
Barium (Ba)	554	Lime Green
Calcium (Ca)	622*	Orange
Lithium (Li)	670	Red

**Note*: Calcium is measured by using the calcium hydroxide band emission at 622 nm as the Calcium main atomic emission occurs at 423 nm.

Over certain ranges of concentration the intensity of the emission is directly proportional to the number of atoms returning to the ground state. This is in turn proportional to the absolute quantity of the species volatized in the flame, i.e. light emitted is proportional to sample concentration. It can be seen that if the light emitted by the element at the characteristic wavelength is isolated by an optical filter and the intensity of that light measured by a photo-detector, then an electrical signal can be obtained proportional to sample concentration. Such an electrical signal can be processed and the readout obtained in an analogue or digital form.

A simple flame spectrophotometer consists of the following basic components:

a. *The burner*: a flame that can be maintained in a constant form and at a constant temperature.

b. *Atomizer and mixing chamber*: a means of transporting a homogeneous solution into the flame at a steady rate.

c. *Simple colour filters (interference type)*: a means of isolating light of the wavelength to be measured from that of extraneous emissions.

d. Atomic Absorption filters are also associated to the instrument to extract the element from the sample and standard solutions

e. Photo-detector: a means of measuring the intensity of radiation emitted by the flame.

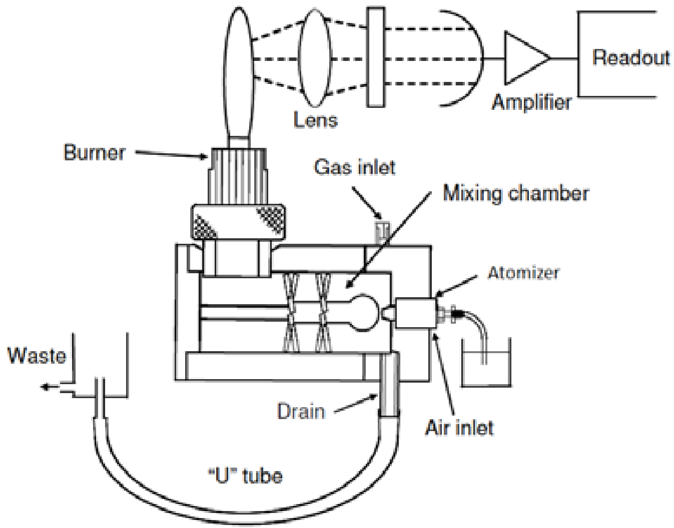


Fig. 26: Basic components of a Flame Spectrophotometer

The analysis of alkali and alkaline earth metals by flame photometry has two major advantages:

i. Their atoms reach the excited state at a temperature lower than that at which most other elements are excited.

ii. Their characteristic wavelengths are easily isolated from those of most other elements due to wide spectral separation.

The analysis of Na, K, Li, Ba and Ca are typically determined at low temperatures, i.e. 1500-2000°C, therefore suitable fuel mixtures are propane/air, butane/air and natural gas/air (but it is suggested that natural gas or LPG must be used other combinations can be harmful and misleading.

Specification

Ranges: - 120-160 mmol/l Na (linearised)

0-10.0 mmol/l K

Limits of Detection

Na	≤ 0.2ppm	-	
K	≤ 0.2ppm	-	
Li	≤ 0.25ppm	Li	≤ 0.25ppm
Ca	≤ 15ppm	Ca	≤ 15ppm
Ba	≤ 30ppm	Ba	≤ 30ppm

Reproducibility: 1% Coefficient of variation (C.V.) for 20 consecutive samples using 10ppm Na set to read 50.0. Readings taken at 20 second intervals.

N.B. C.V. is defined as: the sample standard deviation X 100

mean reading

And sample standard deviation as:

$$\sqrt{\frac{\overline{X}-X^{2}}{n-1}}$$

Where the reading, x is the mean readings of the series and n is the number of readings.

Linearity: Better than 2% when concentration of 3ppm Na and K and 5ppm Li are set to read 100.

Specificity: Interference from Na, K and Li when equal in concentration to the test element will be less than 0.5%.

Stability: Better than 2% over 5 minutes when continuously aspirating 10ppm, sample set to read 50.0. Zero drift better than 2% per hour[1].

Sample Requirements: Between 2 and 6ml/minute.

Recorder Output: Nominal 1.00 volt for readout of 100.0.

Warm Up: The flame must be alight for at least 15 minutes to ensure achievement of the above stated specifications.

Services: Electrical: 90-125V or 190-250V @ 50/60Hz.

Air: Moisture and oil-free 6 litres/minute at 1kg/cm2 (14psi).

[1]N. B. Note warm up requirement.

Instrumental Chemistry

Fuel: natural gas or L.P.G.

Operating Environment: 15°C to 35°C

Instructions for Use of Fotoflame Spectrophotometer

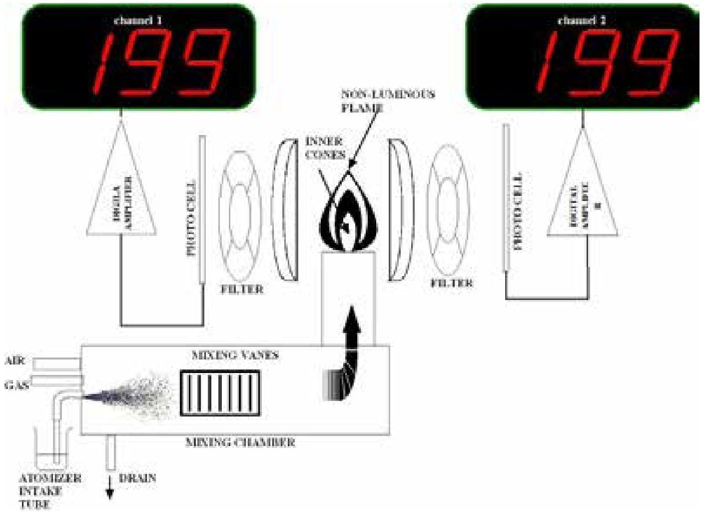


Fig. 27: Showing the Schematic Diagram of the Aimil Photo flame Flame Spectrophotometer

Fig. 27A & 27B: Showing the Front Panel and the back side of the Flame Spectrophotometer and its compressor

General Description

The FOTOFLAME FLAME SPECTROPHOTOMETER is suitable for estimation of alkali metals and alkali earth metals. The equipment is normally supplied with filters for determination of Sodium and Potassium. It works on the principle that when a solution of the metallic salt is sprayed into a non-luminous flame, the flame emits light of a characteristic wavelength. The intensity of this emission is proportional to the concentration of the metal in the solution.

Fig. 27C: The Atomizer intake of the Flame Spectrophotometer

The general layout of the instrument is shown if Fig. (27), Gas and air are introduced at a controlled rate into the mixing chamber (3). The air, while flowing into the chamber, draws in the liquid (1) through the capillary (fig. 27c) and atomizes it into a fine spray. The mixture of gas, air and atomized liquid is ignited at the burner top (5). The excess liquid which has not atomized properly is drained off from the mixing chamber. The light emitted from the flame passes through the lens (9) and filter (10) and then falls on the photocell (11). The filter transmits only the wavelength characteristic of the element being estimated. The output from the photocell is fed to the amplifier (12) and the amplified signal is measured on a Digital Display reading up to 199.

In the DUAL CHANNEL version of the instrument, there is another set of Lenses, Filter and Detector as marked (9A, 10A & 11 A). A separate amplifier (12A, fig. 27) and Display (13A, .Fig. 27) is used for this channel. Normally, the 'K' (Potassium) filter is fixed in this channel whereas the four position filter disc (10, fig. 27) holds the Na and other filters. Both displays in this unit are Digital (0 to 199) and have separate Zero & Sensitivity controls.

The approximate concentrations required for obtaining 100 0n displays are as follows:

Sodium	4 ppm
Potassium	2 ppm

Higher concentrations can also be estimated, but it is not advisable to use very concentrated solutions as this saturates the flame and gives non-linear results. It is preferable to draw a calibration curve for one particular range of concentrations and the solution to be estimated should be diluted to fall within this range.

The atomizer takes up liquid approximately at the tare of 5 ml. per minute, and as it is possible to take a reading in about 20 seconds, only 1 or 2 ml. of the sample is consumed.

Main Features

1. **Electrical Ignition**: An electrical system is provided. Pushing in the knob (3, Fig. 2) switches on the current to the ignition filament and at the same time brings it, into position over the burner top. When the flame ignites and the knob is released, the filament current is automatically switched off and the filament also springs back away from the flame.
2. **Viewing Window**: A viewing window (11, Fig. 27) is provided at eye-level to the seated operator of the instrument. This window enables the operator:
   (a) to see the operation of the ignition filament.
   (b) to watch the flame when making the necessary gas and air adjustments.
   (c) to watch the colour changes in the flame when the test solution is being fed through the atomizer intake-this last giving an immediate indication of clogging of the intake capillary which may occur from time to time.
3. **Sensitivity Control**: The sensitivity control (4, Fig. 27) is the gain control of the amplifier which gives a fine control of sensitivity, and a High/Low switch is provided on the main panel, the two enabling accurate setting of 100.
4. **Stabilised Amplification**: The solid state amplifier uses IC only. The D.C. supply to the amplifier is also regulated by IC This is a special low level amplifier which is designed to ensure linear amplification of the Photocell response.
5. **Rotating Filter Mount**: The filters for use with Sodium and Potassium respectively are mounted on a rotating disc within the unit itself safe from dust, scratches and misplacement or loss. The knurled edge of the disc (2, Fig. 27) showing through the cover enables it to be turned to the required setting when the symbol corresponding to the element being estimated shows on top and an internal spring catch engages and holds the disc in position. A maximum of four filters can be accommodated in the disc.

Setting Up

(1) Connect a tube to the drain outlet nipple on the bottom back right side of the unit. This tube should be long enough to reach the disposal point and should be progressively sloping downwards. Four cups are provided for use under the feet of the instrument, to raise the unit and provide adequate slope to drain excess liquid. These may be used if necessary. To prevent liquid buildup in the chamber, the drain is provided with overflow holes. If there is inadequate drainage, water will overflow and collect under the unit. If there is continuous overflow of water from the drain channel, place a Petri dish under the drain outlet to collect the overflow. Empty this periodically.

> *In the DUAL CHANNEL unit, K filter is fixed into the second channel. The Na and other filters (where ordered) are fitted on the Filter Disc.*

> ***Warning**: The gas and air inlets are marked clearly. The Connections must be made correctly and checked before turning on the air supply. Otherwise the instrument will be damaged. Explosions can occur.*
>
> *The instrument works on bottled gas (LPG krebson) etc.) as well as on laboratory gas supply, the pressure of which should not be less than 12 cm. of water-gauge. Acetylene or compressed Oxygen should never be used on this instrument as both will cause explosion and damage.*

(2) Place the chimney top (Fig. 27) in the recess on the top.

(3) Connect the nipples at the back of the unit to the gas and compressed air supply by suitable lengths of rubber tubes.

Instrumental Chemistry

(4) Remove the plastic shield (6, Fig. 2) (2 thumb nuts on the right of the instrument) used in transit and replace thumb nuts on cover plate.

(5) Connect the 3-pin plug to the mains 230V. A.C., 50Hz., single phase. Ensure proper earthing is available.

(6) Connect the Compressor to the mains.

(7) Fit the atomizer intake P. V. C. tube to the atomizer, sliding it on to the tip of the atomizer needle.

Operation

(1) Switch on the mains using the switch provided at the back of the instrument.

(2) Set the appropriate filter in position by rotating the filter drum till the spring loaded catch engages the disc with the appropriate symbol (K-potassium, Na-Sodium or Ca-Calcium) showing on top.

(3) Put a beaker containing distilled water under the atomizer intake tube and raise it till the tube dips into the water.

(4) Turn on the compressed air supply by starting the compressor.

(5) Adjust the air pressure to about 2 P.S.I. (0.125 Kg.lsq. em.) by means of the air control valve (8, Fig. 27) (turning it clockwise reduces the air supply).

(6) Close the gas valve by turning it clockwise until the end stop is reached. Now turn it one turn anti-clockwise.

(7) Push the ignition knob (3, Fig. 27) in. This brings the filament in position for ignition as well as switches on the mains to the primary of the low voltage transformer which supplies the heating current to the filament. The filament will be seen glowing near the edge of the burner when seen from window (11, Fig. 27).

(8) Now turn on the gas supply. The flame should now ignite. This can be observed through the viewing window (11, Fig. 27). If it does not ignite, open the gas control valve (9, Fig. 2) by turning it anti-clockwise till the flame ignites.

The electrical ignition system will not work if the mains voltage is low as the filament will not reach to the ignition temperature. In such a case the flame could be ignited by introducing a lighted taper inside the chamber through the chimney. It may take 10-15 seconds for the gas to reach the burner top and ignite. If it does not ignite in this time, turn off the gas mains, wait a few minutes to allow the collected gas to dissipate. Try once again by manual ignition with a lighted taper.

Do not put the gas supply on before the filament is seen glowing hot or lighted taper is introduced into the chamber as this may result in collection of gas inside the instrument and cause explosion.

(9) Adjust the air pressure to about 10 p.s.i (see red mark on the dial) (0.7 Kg./sq. cm.) and then adjust the gas flow by operating gas control valve (9, Fig. 27) to obtain a NON LUMINIOUS BLUE FLAME WITH WELL DEFINED GREENISH BLUE INNER CONES SETTLED ON THE GRID HOLES ON THE BURNER TOP(see fig. 27E1). Such a flame is stable and suitable for measurements. With a rich mixture Le. increased gas supply; the inner cones will elongate and merge into each other making the flame luminous, while with lean mixture Le., decreased gas supply, these cones will change to bluish violet, the flame will become unstable and noisy before lifting up from the

Fig. 27D: Showing the Burner and the filter from the top. (Left)

Instrumental Chemistry

Fig. 27E1: Showing the Non-luminous flame (middle)

Fig. 27E2: Showing the flame after the absorption of the standard (right)

burner top and blowing off. While making these adjustments the flame should be watched from the observation window and the gas and air controls should be operated slowly and gradually.

In case flame blows off, shut the gas supply from the source, reduce the air pressure to about 2 p.s.i and follow the ignition procedure given in (7) and (8). If the air pressure is not reduced to 2 p.s.i the filament may not reach the ignition temperature because of the cooling caused by the strong draft of air.

(10) Wait for 5 minutes for the flame to stabilize and then replace the distilled water by a reagent "blank".

(11) Adjust the Display reading to zero (with sensitivity control turned clockwise) by means of the zero control knob (5, Fig. 27)

(12) Replace the reagent "blank" by a "standard" solution with highest concentration in the range of estimation and adjust the sensitivity control (4, Fig. 27) to get 100 on Display.

(13) Feed the reagent "blank" and re-adjust zero if necessary.

(14) Feed the "standard" and again adjust the reading to 100, if necessary by using the sensitivity control.

(15) Recheck the zero reading once again with "blank".

(16) Feed the sample solution and take the reading on the Display.

To use both channels simultaneously in the DUAL CHANNEL unit, repeat steps 10 to 15 with the second channel as well. It is preferable to flush the system with distilled water or reagent "blank" between each sample, especially after estimating a concentrated sample. It is not necessary to flush the system if samples of nearly similar concentration are being examined in quick succession.

Operation Precautions

1. The fuel gases used in the flame photometers are inflammable and therefore potentiallyhazardous. Cylinders of fuel gas should always be stored and used in line with the supplier's recommendation.
2. It is possible that a small quantity of fuel will escape from the instrument during the ignition sequence. The amount of fuel is harmless although may smell slightly. If the smell of fuel gas persists the instrument should be immediately shut down and the source of the leakage determined by using a soap solution on the hose joints.
3. Do not leave the instrument running unattended while the flame is alight.
4. The top of the instrument chimney unit becomes very hot when running and can cause severe burns if touched.
5. The exhaust gases from the flame are very hot and the area approximately 1 metre above the chimney must be avoided. Never attempt to look down the chimney whilst the flame is running. Always use the inspection window.
6. The instrument uses potentially hazardous electrical supplies. Never remove covers from the instrument without first ensuring that it has been isolated completely from the AC mains supply
7. If the instrument is used in a pathology laboratory, all samples should be handled with the caution normally accorded to those known to contain pathogenic organisms. Care should also be taken when undertaking maintenance on instruments that have been used in these environments. A bactericidal agent should be used when cleaning parts

Instrumental Chemistry

during routine maintenance.

Good practice guidelines

1. It is most important that the nebuliser, mixing chamber and burner are kept clean by carrying out the correct shutdown procedure and by periodic maintenance. If high salt solutions are aspirated, correspondingly longer periods should be spent aspirating deionised water prior to shutdown.
2. It is recommended that blank and standard solutions should have a wetting agent (e.g. EMARK DEIONIZED WATER OR DEIONIZED WATER PREAPRED IN LAB added to promote good stability and self cleaning. Any such wetting agent should be non-ionic and used at a concentration of 0ppm. It should be added to the blank, standards and samples at the same concentration.
3. Take care when preparing standards. The performance of the instrument depends upon the accuracy and purity of the calibration standards.
4. If standard solutions are required to be stored for any length of time or at an elevated temperature, a suitable mould inhibitor e.g. azide should be added. However if this contains the element to be measured (e.g. sodium) it is important that the samples also contain an equivalent amount.
5. Always sample from the top half of the sample container. The bottom half may contain sediment or particulate matter which could easily block the fine tubing used in the atomizer
6. Always use recommended spares. Even where an alternative part may be obviously suitable there may be good reasons for not using it.
7. Never use glass containers to store calibration standards.

Calibration

The output from the photocell measured as the reading on Display is linear with reference to the intensity of emission. But the relation between the concentration of the solution and the intensity

of emission may not necessarily be linear. It is, therefore, necessary to draw a calibration curve by using solutions of known concentrations for a particular range. The samples to be estimated should lie within this range.

A 4 ppm sodium chloride solution is applied after the instrument has aspired a 2 ml of distilled water the display is adjusted to 100 and again the distilled water is aspired to read the display as 000 the instrument is calibrated

It is important to understand that the principles of flame photometry are such that, over certain concentration ranges, light emitted from the flame is directly proportional to the concentration of the species being aspirated. The graph below shows that the direct relationship between the flame emission and concentration is only true at relatively low concentrations. Above these low levels the flame begins to saturate and the flame emission ceases to increase in a linear relationship to concentration.

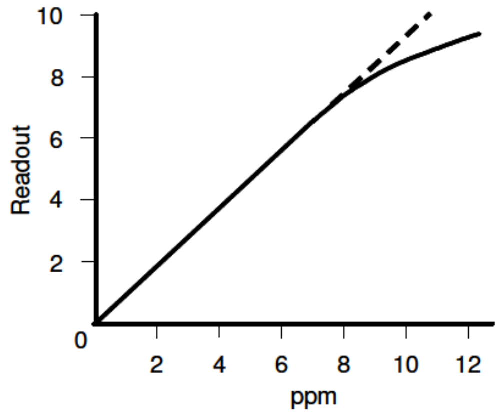


Fig. 28: Relationship between sample concentration and flame emission.

If the samples being analysed lie on the linear part of the curve then the user can take direct concentration readings from the digital display. If, however, the concentration of samples are above the levels shown on the graph then the user has the choice of either:

a. diluting the samples so that they lie on the linear part of the curve, or

Instrumental Chemistry

b. constructing a calibration curve and relating the digital display reading to the concentration by cross-reference to the curve.

A calibration curve is prepared using standard solutions containing known concentrations of the elements to be determined and if necessary, other materials to ensure that the standard and sample backgrounds match. The concentration range covered by the calibration curve will depend upon the expected concentration of the samples so that the sample readings fall somewhere in the middle of the calibration curve. Once the calibration curve has been plotted, the readings for the sample solutions are compared with the curve to allow the sample concentrations to be established. It is important to realize that each element has its own characteristic curve and separate calibration curves must be constructed.

If the same estimation is performed on a routine basis, the calibration curve need only be prepared once and checked periodically. Instrument re-calibration is easily achieved by setting the blank solution to read zero and the top standard to read the same value as it did when the calibration curve was initially prepared. The graph in Figure 29 shows a typical curve obtained when measuring in parts per million (ppm).

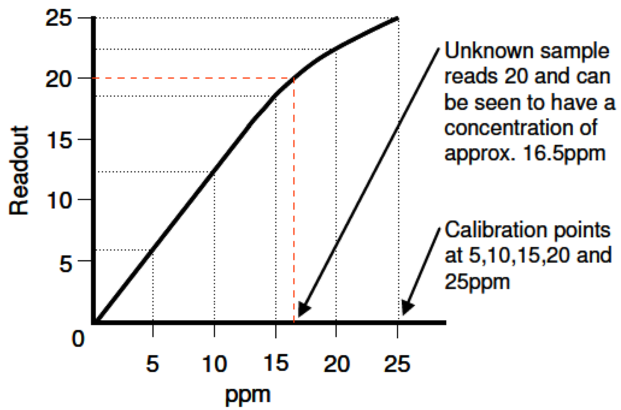


Fig. 29: Typical calibration curve measuring ppm

The peoples working in medical environments are quite likely to be using the S.I. unit of mmol/l to report their results. The ppm to

mmol/l can be obtained by a simple calculation formula:

$$\text{mmol} = \frac{\text{ppm}}{\text{atomic weight}}$$

The relationship between mmol/l and ppm is defined below:

Sodium Na 1ppm = 0.0435mmol/l 1mmol/l = 23ppm

Potassium K 1ppm = 0.0256mmol/l 1mmol/l = 39ppm

Lithium Li 1ppm = 0.1441mmol/l 1mmol/l = 7ppm

Calcium Ca 1ppm = 0.0250mmol/l 1mmol/l = 40ppm

This relationship means that Na and K samples in the normal clinical range of 136-145mmol/l

Na and 3.5-5.0mmol/l K should be pre-diluted 1 in 100 or 1 in 200 to get optimum results from the flame spectro-photometer.

1. Aspirate a blank solution and set the readout to 000 using the blank control.
2. Aspirate the highest standard solution and set the readout to an appropriate reading using the sensitivity controls. Re-check the blank setting and adjust if necessary.
3. Aspirate the remaining standard solutions (if used) to construct the calibration curve and note the results.
4. When the blank and standards are set, unknown samples can be aspirated and the results noted, either directly from the instrument readout, or by deriving the concentrations from the calibration curve.
5. Calibration needs to be checked periodically by aspirating the blank and standard solutions. Initially this check should be carried out after every 10 samples. Experience and increased confidence in the PFP7 will enable you to best judge the frequency of this check.
6. The decimal point (d.p.) switch can be set to illuminate the decimal point in any significant position. This should be chosen to give sufficient resolution for the test required.

Switching Off

Before switching off, flush the system clean with distilled water. In routine course, the air and gas controls should

This is very important do not make it reverse

be left undisturbed and the air and gas should be turned off at the source.

Follow the sequence below in turning off gas and air.

(1) Turn off the gas, the flame will extinguish.

(2) Turn off the air.

(3) Switch off the mains.

Maintenance and Servicing

The most important aspect of maintenance is to keep the atomizer, mixing chamber, burner and optical assembly clean for reliable and accurate results. Apart from this, very little attention is required except when there is a component failure. The appropriate procedures for this work are given below:

Cleaning atomizer needle and intake capillary: Normally flushing with distilled water and introducing the cleaning wire is all that is required to remove any solid particles which might be present in the solution. In case these fail to clear the blocked orifice, proceed as follows:

The Atomizer is a straight plug with two '0' rings for sealing and a screw cap to hold it in place. No force needs to be used to insert or remove the Atomizer. Once the screw cap is unscrewed, the atomizer plug can be removed by gentle handling. The Atomizer itself is made of a special epoxy resin. For cleaning the Atomizer, either detergent solution, or an organic solvent like Xylene may be used. Do not use mechanical means to clean the atomizer since this may lead to an increase or change in the small air holes which are of critical dimensions.

Preparation for Analysis

Calibration standards

A comprehensive range of aqueous calibration standards is available from Emark in both industrial and clinical levels. These must be diluted to a suitable concentration for aspiration into the flame-

Clinical Standards (500ml)

1.00mmol/l Li

100mmol/l Na, 100mmol/l k

140mmol/l Na, 5mmol/l k

120mmol/l Na, 2mmol/l k

160mmol/l Na, 8mmol/l k

160mmol/l Na, 80mmol/l k

Industrial standards (500ml)

1000ppm K

1000ppm Li

3000ppm Ba

1000ppm Na

1000ppm Ca

When preparing standards always observe the following:

1. Standards must always contain the constituents that are present in the samples in the same concentration ratios; i.e. if samples are prepared in 0.05M HCl then the standards should also contain 0.05M HCl.
2. Always ensure that the standards encompass the expected range of the sample concentrations.
3. Standards should be prepared so as to ensure that the region in which measurements are made coincide with the concentrations that produce the optimum performance from the flame photometer, i.e…
    - …when measuring sodium, the top standard is ideally 10ppm,
    - …when measuring potassium, the top standard is ideally 10ppm,
    - ...when measuring calcium, the top standard is ideally 100ppm,
    - …when measuring barium, the top standard is ideally 1000ppm,
    - …when measuring lithium, the top standard is ideally 10ppm.

A minimum of four standards should be prepared to enable an accurate calibration curve to be constructed[2].

Since a flame spectrophotometer measures the concentration of

the element itself in solution, standard solutions prepared from the salts of sodium, potassium, lithium, calcium and barium must be made up to contain the concentrations required in terms of the quantity of the elements. Below are two examples of how to prepare standards of 1mg Na/100ml (10ppm Na) and 1mg K/100ml (10ppm K).

Preparation of Standards

Sodium

Accurately weigh 5.85 of dry "Analar" quality NaCl, dissolve in pure deionized water and wash into a 1000ml volumetric flask. Fill to the mark with pure deionized water. To prepare the standard solution for use with the flame photometer, this stock solution should be diluted 1 in 50.

Calculation :

Atomic weight of Sodium = 23

Molecular Weight of Sodium Chloride = 58.4

$\therefore$ 5.8 gm of Sodium Chloride will contain $\frac{5.85 \times 23}{58.46}$ = 2.3015gm/L of Sodium

Thus in 1000 ml of solution there is 2.3015gm Na or .23015mg Na/100ml.

Diluting 1 in 50 gives a standard of 4.603mg Na/100ml = 40ppm Na. approx.

Now to make a 4ppm standard sodium solution this is diluted again to 1 in 10

Potassium

Accurately weigh 3.73gm of dry "Analar" quality KCl, dissolve in pure deionized water and wash into a 1000ml volumetric flask. Fill to the mark with pure deionized water. To prepare the standard solution for use with the flame photometer, this stock solution should be diluted 1 in 50. (calculate using the same calculation formula as above)

Storage

Store solutions away from direct sunlight in a cool place, ideally at temperatures below 25°C.Glass containers should not be used for storage as they can affect the sodium concentration levels. Standards should be stored in sealed, plastic vessels and in high concentrations,

[2]*Note*: The blank used should contain all the constituents of the standard solutions except the element being measured.

(e.g. as a stock 1000ppm solution) and dilutions prepared as required. The long-term storage of low concentration standards is not recommended due to degradation of ionic species.

Method 2

A simple standard can be made by adding 5.85gm of sodium chloride in 1000ml of distil water that will give a 100mEq/lit of sodium chloride And similarly 3.73gm of potassium chloride in 1000ml of distill water will give 5molEqv/l of potassium chloride. Then diluting these standards according to the table below:

Solution No	Sodium Stock (ml)/500ml(dW)	Potassium stock (ml)/500mlDW	Na^+conc mEq/L*	K^+conc meqv/L**
1	1.4	2	.28	.02
2	1.5	3	.3	.03
3	1.6	4	.32	.04
4	1.7	5	.34	.05
5	1.8	6	.36	.06
6	1.9	7	.38	.07
7	2.0	8	.40	.08
8	2.1	9	.42	.09

*For sodium divide the dilution aliquot by 5 since it is diluted 5 times (100 in 500ml) but its original standard is 100

**For Potassium divide the dilution aliquot by 100 since it is diluted 5 times (5 in 500ml) but the original standard was 5

To find out the Sodium Potassium and Lithium equivalent of the Standard Solutions

Molecular Equivalent of the Standard Solution

$$= \frac{\text{Molecular Equivalent of the Standard Solution}}{\text{Atomic weight of the respective element}}$$

Sample preparation

There are several practical points regarding sample preparation, which should be adhered to in order to achieve the required accuracy in your analysis:

1. Avoid handling samples with fingers. This leads to serious contamination, e.g. if a finger is immersed in 20ml of deionized water the resulting Na concentration will exceed that of a 10ppm standard.
2. All analyses involve the use of a diluent, which is almost

always deionised water. This should be of the highest quality for accurate flame analysis. Sodium, potassium and calcium are present in high concentrations in tap water and thus efficient deionisation is essential.

3. Species that cause interference should be removed from samples or the equivalent concentration of the interferant should be present in the standards so as to avoid erroneous results, e.g. if a sample of approximately 10ppm Na contains approximately 1000ppm Ca, then Na analysis can only be achieved by removing the Ca with oxalate/oxalic acid or ensuring all standards contain 1000ppm Ca.
4. Always try to follow a well-documented analytical procedure, which should contain information pertaining to interference removal when applicable.
5. Standards and samples should not be exposed to the atmosphere for long periods due to contamination from airborne particles and the evaporation of the solvent that could lead to elevated concentrations.

Sample Extraction

A number of methods for extracting sodium, potassium, lithium, calcium and barium from a wide variety of raw materials may be obtained by using the calculation systems shown above The sample must be in the form of an aqueous solution, with no solid matter present, to be suitable for direct introduction into the flame photometer. This is achieved by:

- Extracting the salts from solid samples using deionized water or suitable extractants e.g. saturated $CaSO^4$ for sodium in soil. Extraction is more successful using a blender, macerator or shaking machine.
- If the sample is organic then the organic material should be removed by ashing. The remaining oxides are then dissolved using strong acids.
- Filtration/centrifugation is used to remove solid debris.

When aqueous, the sample can then be diluted to a known, accurately measured volume using deionized water. If it is a concentrated sample then the dilution ratio should be increased. If the sample concentration is low then a small volume of diluent and

initial extractant should be used. Whichever method of extraction is used, the resultant solution must always be free of any particulate matter that may cause blockages in the atomizer capillary tube.

Dilution

In order to obtain samples and standards of the right concentration for aspiration into the flame, various levels of dilution will often be necessary. Good quality deionized water should normally be used for carrying out these dilutions and it is recommended that the same batch of waters should be used for diluting the samples and standards.

Determination of Alakli Metals Using the Flame Spectrophotometer

Investigation of some factors affecting accuracy of sodium determination and their application in the determination of sodium by Flame Emission Spectroscopy

Introduction

Atomic emission spectroscopy (AES) employing flames, also called flame emission spectroscopy (FES) or flame photometry has found widespread application in elemental analysis (1). Its most important uses have been in the determination of sodium, potassium, lithium and calcium, particularly in biological fluids and tissues. For reasons of convenience, speed, and relative freedom from interferences, flame emission spectroscopy has become the method of choice for these otherwise difficult to determine elements. The method has also been applied, with varying degree of success, to determine of perhaps half the elements in the periodic table. Flame photometry is based on the emission spectrum of an element which is excited in a flame (e.g. propane/air, acetylene/air) which is hot enough to cause the element to allow emission of characteristic radiation. The spectrum may be relatively simple, consisting of only a few lines, or may be complex, broad bands. Measurement of the intensity of a portion of a spectrum characteristic of an element can provides a measure of the concentration in the sample. The required spectral line or a portion of the spectrum is isolated either by a monochromator or by an optical filter. The intensity of the isolated radiation is measured by a photosensitive detector coupled to an

Instrumental Chemistry

amplifier and recorder.In the analysis of sodium and potassium in the presence of calcium, some interference by the latter occurs, due to spectral overlap. The addition of a sufficient quantity of aluminium ions to the analyte solution tends to reduce the emission due to calcium and hence minimize the interference (2, 3).

Potassium determination by flame emission is affected mainly by ionization of potassium at the high temperatures associated with air/acetylene or hotter flames, especially at low concentrations of the elements. However this effect is neglible in the air/propane flame used by the flame analyser in this experiment. Therefore, addition of radiation buffers is not required for potassium analyses with this instrument.

Experimental Procedures

1. Optimization of the fuel/air flow rates for determination of sodium:
   - (a) Prepare a calibration series containing 1.25, 2.5, 5.0 and 7.5ug/mL sodium respectively in distilled water (25mL each), using the 50ug/mL standard sodium solution provided.
   - (b) Set the sodium filter in position before the photocell and set the air pressure to the burner as recommended(10p.s.i)
   - (c) Depress ignition switch to light the flame and slowly increase the fuel flow rate. Once the flame is lit, observe the flame, and carefully adjust the fuel flow rate, until a non- luminous flame is obtained. Allow the system to equilibrate for about 15min.
   - (d) Aspirate the 2.5ug/mL sodium standard and adjust the sensitivity knob to obtain an emission reading of about 30 units. Re-zero the instrument while aspirating distilled water.
   - (e) Aspirate again the 2.5ug/mL solution, and carefully change the fuel flow rate until a maximum signal is obtained. Avoid using a luminous flame, which creates a high background signal.
   - (f) Re-zero with distilled water again. The instrument is now ready for use.

(2) Investigation of effect of aspiration rate on emission signals of sodium:
   - (a) Into each of four 25mL volumetric flasks, pipette the required volume of standard 100ug/mL sodium standard, to give a final concentration of 2.5ug/mL.
   - (b) Add to the flasks 2.5, 5.0, 7.5 and 10mL respectively of ethanol and make up to the mark with distilled water. These correspond to 10 to 40% by volume of ethanol in sodium solutions. Similarly prepare a series of 10-40% ethanol blank solutions in distilled water.
   - (c) Using distilled water, zero the instrument and then aspirate the 2.5ug/mL sodium standard in distilled water (0% EtOH), noting its emission value.
   - (d) Aspirate and measure the emission intensities of the distilled water sodium standards (1.25 to 7.5ug/mL).
   - (e) Aspirate the ethanol samples in order of increasing ethanol content, and note the corresponding readings.
   - (f) Plot emission vs ethanol (0-40% v/v) content of the solution, corrected for blanks.
   - (g) Exercise: What precautions should be taken when determining sodium in alcoholic beverages?

(3) Interference of sodium emission by calcium and the countering effect of aluminium:
   - (a) Into five 25mL volumetric flasks, add the required volume of the 100ug/mL sodium standard stock solution that will give respective final concentration values of 1.25, 2.5, 5.0, and 7.5ug/mL.
   - (b) To each flask, add 10mL of the 1000ug/mL calcium standard stock solution provided and make up to the mark with distilled water.
   - (c) Prepare a blank solution containing 10mL of the 1000 ppm calcium stock solution in 25mL solution.
   - (d) Into five other 25mL volumetric flasks, add similar quantities of sodium and calcium solutions. Then add to each, 5mL of the aluminium solution provided and make up to the mark with distilled water.

Instrumental Chemistry

(e) Prepare a blank containing 10mL of 1000ug/mL calcium standard stock solution and 5mL of the aluminium solution in 25 mL solution.

(f) Aspirate in the following order:

(i) The standard solutions in distilled water (1.25-7.5ug/mL), with distilled water as blank.

(ii) The sodium-calcium solutions (1.25-7.5ug/mL)and blank.

(iii) The sodium-calcium-aluminium solutions (1.25-7.5ug/mL) and blank.

(iv) Sample solutions and blank (preparation in later section).

(v) The sodium-ethanol solutions and blanks.

(vi) Tabulate the emission readings. Note the change of color of the flame in the three types of solutions.

Exercises

(A) Plot blank-corrected emission values vs sodium concentration of each set of solutions (i), (ii) and (iii) on the same sheet of graph paper, or using a plotter.

(B) Comment on the coincidence of the calibration curves, and the effectiveness of the Al+3 in suppressing Ca+2 interference.

(C) Plot the emission values for the sodium-ethanol solutions, corrected for ethanol- water blanks, vsC2H5OH (ethyl alcohol) concentration.

Analysis of Sodium in Sample

(a) Place triplicate, accurately weighed or measured quantities of the sample provided into separate boiling tubes.

(b) To each tube add 5mL conc. nitric acid and reflux at 135-140°C for 1h. in a fume hood.

(c) Prepare an acid blank simultaneously

(d) Cool and dilute with 10mL distilled water

(e) Filter into 100mL volumetric flasks and make to volume with distilled water rinses of the boiling tubes and filter papers.

(f) Aspirate your sample solutions along with the solutions of section and determine the mean sodium content of the samples.

Calculations for (alternative method)

Examples:

The Higher dilution reads:	149 (RS2)
The Lower Dilution reads:	114(RS1)
The sample reads :	140(RT)

The sodium equivalent of the higher dilution: -4.34 (from the formula Shown above)(CS_2)

The sodium equivalent of the lower dilution: -.043(from the formula shown above (CS_1)

The Sodium present in the sample

$$\frac{CS_1 + (RT - RS_1)(CS_2 - CS_1)}{RS_2 - RS_1}$$

$$\frac{.043 + (140 - 114)(4.34 - .043)}{149 - 114}$$

$$.\frac{043 + 26 \times 4.297}{149 - 114} = \frac{111.765}{35} = 3.19 meqv / lit$$

The potassium and lithium can be determined by the same formula but three things must be kept in mind

1. Use the respective filters
2. The potassium filter is associated in the second channel of the flame spectrophotometer and
3. During the potassium and lithium reading the respective potassium and lithium equivalents must be calculated by using the same formula shown above.

11

The Viscosity of Liquids

After studying the present lecture, you will be able to

Define viscosity and viscosity coefficient

Outline the method to measure viscosity using Ostwald viscometer

Determine the average molecular weight of a polymer

Determine the surface concentration of 1-butanol in aqueous solution

Measure the distribution coefficient of a solute between two solvents

Introduction

Viscosity, one of the transport properties, arises because of intermolecular attractive and relatively long-range forces. Viscosity coefficient (η), a specific constant characteristic of a liquid could be expressed by the following equation of Poiseuille.

$$\eta = \frac{P\pi r^4 t}{8LV} \tag{1}$$

where V is the volume of liquid delivered in time t, through a capillary of radius r and length L, with a hydrostatic pressure P.

In an apparatus designed so that equal volumes of liquids can flow through the same capillary of length L and radius *r*, η may be written as

$$\eta = k'hdgt \tag{2}$$

If g remains constant in any given location and *h*, the height through which the liquid falls is kept constant, above equation becomes,

$$\eta = ktd \tag{3}$$

where k is the dimensional constant of the apparatus.

If two liquids are compared using the same apparatus, it follows that

$$\frac{\eta_1}{\eta_2} = \frac{d_1 t_1}{d_2 t_2} \quad (4)$$

If , the coefficient of viscosity of one of the substance, is known from a previous measurements, then , the viscosity of the other liquid, can be calculated from the measured quantities, d_1, d_2, t_1 and t_2.

Viscosity Measurement of a Liquid

The viscosity of two liquids can be compared by making use of an Ostwald Viscometer which consists of two bulbs, one attached with a capillary tube and U-tube below the capillary tube while other bulb is attached to the other arm of u-tube at a level lower than the other bulb. The liquids of known densities are allowed to flow through the capillary maintaining the same differences of levels in the limbs and the time equation which governs the flow lead to the relation:

$$\frac{\eta_1}{\eta_2} = \frac{t_1 d_1}{t_2 d_2} \quad (5)$$

where η_1 and η_2 are viscosity coefficients of the liquid and water, respectively. d_1 and d_2 are the densities of liquid and water, respectively. Knowing the value of viscosity of one liquid, one can calculate the viscosity of other liquid.

The procedure for measurement of viscosity is as follows. The viscometer is fixed vertically on the stand and 10 mL or 20mL of water is pipetted into the lower bulb. The volume of water (10 mL or 20 mL) is chosen so that the liquid can be conveniently sucked into the upper bulb leaving some in the lower bulb. It is sucked up into the other bulb to a point about the mark above the bulb. Now it is released and stop clock is started when the meniscus crosses the mark. The clock is stopped when the mark below the bulb is passed. The time is recorded at the moment. The same procedure is repeated twice or thrice and their average is used in calculations.

Similarly, the experiment is repeated with the given liquid. Using the specific gravity bottle, one can determine the specific gravity of

the liquid and calculate the viscosity. The viscosity of water at room temperature is used from the tables.

Experiment: to determine the average molecular weight of the polymer

Viscosity of a polymer solution could be studied to determine average molecular weight of the polymer. An average molecular weight is calculated because the polymer molecules do not all have the same mass.

Empirically it has been found that the intrinsic viscosity is sensitive both to the shape and molecular weight of the macromolecular solute. The equation used by Mark-Houwink relation,

$$[\eta] = KM^a \quad (6)$$

where M is the average molecular weight and K and a are constant for a given solvent-solute system. The constant a is sensitive to the shape and varies from zero for hard sphere or 0.5 for random coils to 2.0 for rigid rods.

Variation of specific viscosity of a solution η_{sp} (specific viscosity or reduced viscosity) is defined as ,

$$\eta_{sp} = \frac{\eta_i - \eta_o}{\eta_o},$$

where η_i the viscosity of solution *i* and η_0 the viscosity of pure solvent) with the concentration of solute is given by the equation:

$$\frac{\eta_{sp}}{c} = [\eta] + Kc\,[\eta]^2 \quad (7)$$

where, c is concentration of the polymer in g/mL and K is a constant.

The determination of average molecular weight of polyvinyl acetate in acetone and methanol uses the following Procedure:

Prepare solution of polyvinyl acetate in acetone containing approximately 1 mg/ mL. From this prepare four more solutions of 0.2, 0.4, 0.6, 0.8 mg/ mL by dilution. Measure the specific viscosity of all the four solutions as described above.

Repeat the above experiment with solution of polyvinyl acetate in methanol.

Plot versus c and calculate and K from equation (2). Also, using the empirical formula (1) and constant of K and a from the table

given below, determine the molecular weight of polyvinyl acetate in these two solvents.

Solvent	K	a
Acetone	21.4×10^{5}	0.68
Methanol	38×10^{-5}	0.59

Excess Surface Energy (Surface Tension)

In this experiment, we study the determination of surface concentration of 1-butanol in aqueous solution

The addition of a surface active agent into any liquid changes the surface tension of a liquid. The change in surface tension is related to the excess surface concentration of the solution by the Gibb's adsorption isotherm:

$$\tau = -\frac{1}{RT} \cdot \frac{d\gamma}{d\ln c} \tag{8}$$

$$\tau = -\frac{c}{RT} \cdot \frac{d\gamma}{dc} \tag{9}$$

where,

τ = surface excess concentration of solute per unit area

R = gas constant

T = absolute temperature

γ = surface tension of the solvent

c = concentration of the solute

The surface tension may be compared with that of pure liquid using a Stalagmometer which is operated on the "drop-weight" principle. The Stalagmometer has a bulb with a capillary attached and marks on either side of the bulb. We let the fixed volume of a liquid flow through the capillary ad count the drops; knowing the densities of liquids, the drops weight and hence the surface tensions, may be compared:

$$\frac{\gamma_1}{\gamma_2} = \frac{n_2 d_2}{n_1 d_1} \tag{10}$$

where γ_1 and γ_2 are the surface tension of water and liquid. d_1 and d_2 are the densities of water an liquid, respectively. n_1 and n_2 are the number of drops of water and liquid.

Procedure

A 4% (v/v) solution of 1-butanol is supplied from which 3%, 2% and 1% solution of 1-butanol is prepared using dilution method. The Stalagmometer is clamped vertically. Water is sucked up into the Stalagmometer from a beaker to a level above the bulb. It is started to release and when the level crosses the mark, counting of the drops is started till the level crosses the lower mark. This experiment is repeated and the average of the reading is taken in calculation. The similar experiment is conducted with each diluted solution and their densities are determined using a specific gravity bottle. The value of is plotted against ln c or the value of γ is plotted against c. From the plot, the slope at two point are found by drawing tangents at c= 1.5% and c = 2.5%.

The surface excess concentration of 1-butanol is calculated from the slope of the curve in each case.

Distribution Coefficient

If in a system of two immiscible or slightly miscible solvent, a substance, soluble in both the solvents is added, then the added substance will distribute itself between the two liquids in a definite manner depending upon its solubility. At equilibrium the ratio of the concentrations of the solute in the two liquids is constant at a given temperature and is called the distribution coefficient or partition coefficient. It is important that the solute must exist in the two solvents in the same molecular state. If C, and C_2 are the concentrations of the solute in the two solvents when equilibrium is reached, then at constant temperature

$$\frac{C_1}{C_2} = \text{Constant, } (K_{part}) \tag{11}$$

Experiment

Determine the distribution coefficient of iodine between carbon tetrachloride and water at a given temperature (or room temperature).

Theory

The molecular state of iodine in both the solvents CCl_4 and water is the same as I_2 and hence the partition coefficient is practically independent of concentration in dilute solutions. Hence, the

distribution law in its simplest form may be applied i.e., $C_{org}/C_{aq} = K_{part}$. (Partition Coefficient)

Procedure

1. By means of a graduated pipette place about 50, 40, 30 and 20 mL of a saturated solution in I2 in CCl4 and properly labelled (1 to 4) glass stoppered bottles. Add approximately 0, 10, 20 and 30 mL CCl4 to bottle nos. 1, 2, 3 and 4, respectively. Add about 200 mL of distilled water to each of the bottles.

2. Stopper the bottles tightly and shake thoroughly. Withdraw 20 mL of the aqueous layer carefully and titrate against 0.01 N $Na_2S_2O_3$ using starch solution as indicator (repeat to concordance). To analyse the lower CCl_4 layer, introduce a dry 5 mL pipette into the bottle while blowing continuously in and lower till the bottom in reached, withdraw 5 mL of the lower layer of CCl_4 and tritrate against 0.1N thiosulphate solution. Calculate the ratio of concentrations.

Similarly, titrate aqueous and CCl4 layer from bottle nos. 2, 3 and 4 and observe that the partition coefficient is reasonably constant. Take the mean value as K_{par}t.

While titrating the non-aqeuous layer, the titration flask must constantly be shaken, otherwise the equivalence point may pass without the disappearance of purple colour of non-aqueous layer. The addition of about 5mL of 10% KI solution also helps. KI facilitates extraction of iodine into aqueous solution during titration due to the formation of unstable complex ion

$$I_3^- \text{ as } I^- + I_2 \Leftrightarrow I_3^- .$$

Exercise

Distribution of succinic acid between water and ether could also be studied. Succinic acid also remains in normal molecular state in both water and ether. Take about 1.0, 1.5 and 2.0 g of succinic acid on three stoppered bottles numbered 1 to 3. To each bottle add about 50 mL ether and 50 mL distilled water. Titrate 10 mL of ethereal layer with 0.05 M NaOH and 10 mL g aqueous layer with 0.5 M NaOH.

Calculate the concentration of the acid in the two layers in terms of moles/ l and obtain the average value of he ratio of concentrations to get Kp$_{art}$.

Application

An experiment using the disbritubion law is discussed below

Determination of the equilibrium constant of the reaction

$$KI + I_2 \rightleftharpoons KI_3 \tag{12}$$

Theory

If iodine is added to a moderately concentrated aqueous solution of KI, it combines with the iodide ion to form tri-iodide ion, I^-_3. Thus, in aqueous KI solution containing iodine, we have the chemical reaction KI + I_2 KI_3 and the equilibrium constant of the reaction is,

$$K = \frac{[KI_3]}{[KI][I_2]} \text{ or } K = \frac{[I_3^-]}{[\bar{I}][I_2]} \tag{13}$$

Since molecular iodine is soluble in both the aqueous and organic CCl_4 phase, it obeys the distribution law whereas KI and KI_3, being the electrolytes, are insoluble in CCl_4.

Procedure:

Proceed as in previous exercise, but use aqueous KI solutions of different concentration in place of water. The aqueous layer will now have more I_2, so the same thiosulphate (say 0.1N) may be used to titrate the two layers. The titre of aqueous layer correspond to total of free I_2 and I^-_3, and the concentration of free I_2 may be calculated using the concentration in CCl_4 layer and the previously determine K_{part}. The initial I- concentration is known and since,

$$[I^-]_{initial} = [I^-]_{equil} + [I_3^-]_{equil} \tag{14}$$

$$\therefore [I_3^-]_{equil} = \left[(\bar{I})_{initial} - \left(\frac{K_{part}}{[I_2]_{org}} \right) \right] \tag{15}$$

Now, using values of (I_2), (K_I) and (KI_3) in aqueous KI layer, the equilibrium constant can be calculated.

Summary

In the present lecture, the experiments on viscosity, surface tension and distribution coefficient were described. The viscosity of two liquids was compared by making use of an Ostwald Viscometer.

Instrumental Chemistry

The use of viscosity measurement to determine the average molecular weight of a polymer was also outlined.

If in a system of two immiscible or slightly miscible solvent, a substance, soluble in both the solvents is added, then the added substance distributes itself between the two liquids in a definite manner depending upon its solubility. At equilibrium, the ratio of the concentrations of the solute in the two liquids is constant at a given temperature and is called the distribution coefficient or partition coefficient. The determination of the partition coefficient of iodine between chloroform and water was described. The partition law was also used to determine the equilibrium constant between KI, I_2 and KI_3.

Standard Laboratory Viscometers for Liquids

U-tube viscometers

These devices also are known as glass capillary viscometers or Ostwald viscometers, named after Wilhelm Ostwald. Another version is the Ubbelohde viscometer, which consists of a U-shaped glass tube held vertically in a controlled temperature bath. In one arm of the U is a vertical section of precise narrow bore (the capillary). Above this is a bulb, with it is another bulb lower down on the other arm. In use, liquid is drawn into the upper bulb by suction, then allowed to flow down through the capillary into the lower bulb. Two marks (one above and one below the upper bulb) indicate a known volume. The time taken for the level of the liquid to pass between these marks is proportional to the kinematic viscosity. Most commercial units are provided with a conversion factor, or can be calibrated by a fluid of known properties. The time required for the test liquid to flow through a capillary of a known diameter of a certain factor between two marked points is measured. By multiplying the time taken by the factor of the viscometer, the kinematic viscosity is obtained.

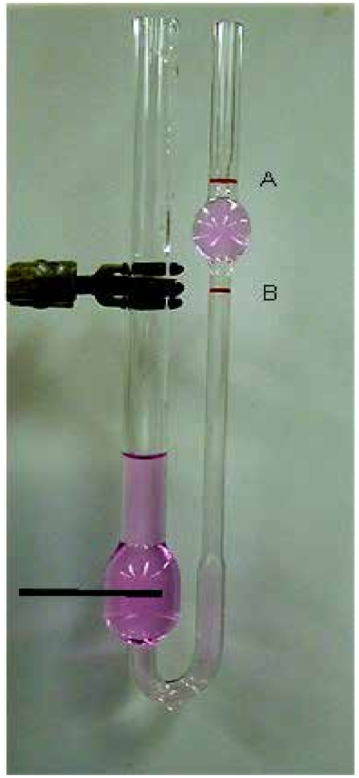


Fig. 30: Ostwald viscometers measure the viscosity of a fluid with a known density

Such viscometers are also classified as direct flow or reverse flow. Reverse flow viscometers have the reservoir above the markings and direct flow are those with the reservoir below the markings. Such classifications exists so that the level can be determined even when opaque or staining liquids are measured, otherwise the liquid will cover the markings and make it impossible to gauge the time the level passes the mark. This also allows the viscometer to have more than 1 set of marks to allow for an immediate timing of the time it takes to reach the 3rd mark, therefore yielding 2 timings and allowing for subsequent calculation of Determinability to ensure accurate results.

Falling Sphere Viscometers

Stokes' law is the basis of the falling sphere viscometer, in which the fluid is stationary in a vertical glass tube. A sphere of known size and density is allowed to descend through the liquid. If correctly selected, it reaches terminal velocity, which can be measured by the time it takes to pass two marks on the tube. Electronic sensing can be used for opaque fluids. Knowing the terminal velocity, the size and density of the sphere, and the density of the liquid, Stokes' law can be used to calculate the viscosity of the fluid. A series of steel ball bearings of different diameter are normally used in the classic experiment to improve the accuracy of the calculation. The school experiment uses glycerine as the fluid, and the technique is used industrially to check the viscosity of fluids used in processes. It includes many different oils, and polymer liquids such as solutions.

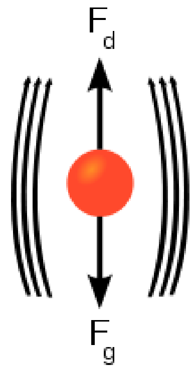


Fig. 31: Creeping flow past a sphere

In 1851, George Gabriel Stokes derived an expression for the

Instrumental Chemistry

frictional force (also called drag force) exerted on spherical objects with very small Reynolds numbers (e.g., very small particles) in a continuous viscous fluid by changing the small fluid-mass limit of the generally unsolvable Navier-Stokes equations:

$$F = 6\pi r\eta v$$

where:

- is the frictional force,
- is the radius of the spherical object,
- is the fluid viscosity, and
- is the particle's velocity.

If the particles are falling in the viscous fluid by their own weight, then a terminal velocity, also known as the settling velocity, is reached when this frictional force combined with the buoyant force exactly balance the gravitational force. The resulting settling velocity (or terminal velocity) is given by:

$$V_s = \frac{2}{9}\frac{r^2 g(\rho_p - \rho_f)}{\mu}$$

where:

- Vs is the particles' settling velocity (m/s) (vertically downwards if $\rho_p > \rho_f$, upwards if $\rho_p < \rho_f$),
- is the Stokes radius of the particle (m),
- g is the gravitational acceleration (m/s^2),
- ρ_p is the density of the particles (kg/m^3),
- ρ_f is the density of the fluid (kg/m^3), and
- μ is the (dynamic) fluid viscosity (Pa s).

Note that Stokes flow is assumed, so the Reynolds number must be small.

A limiting factor on the validity of this result is the roughness of the sphere being used.

A modification of the straight falling sphere viscometer is a rolling ball viscometer which times a ball rolling down a slope whilst immersed in the test fluid. This can be further improved by using a patented V plate which increases the number of rotations to distance traveled, allowing smaller more portable devices. This type of device is also suitable for ship board use. Currently, new equipment is

developed for viscosity measurements. This equipment is survismeter and not only measures viscosity only but along with viscosity, it also measures surface tension, interfacial tension, wetting coefficient with high accuracy and precision. The survismeter also measures a new parameter which is noted as friccohesity. The friccohesity establishes an interface between the cohesive forces and the frictional forces within the similar or dissimilar molecules, dispersed in desired medium. Friccohesity is intimately associated with distribution of the particles due to oscillations of the velocity components on gaining kinetic energy. *Since friccohesity depicts demonstration of cohesive or potential forces and kinetic or frictional forces together and thus the particle distribution is automatically involved in the behavior of the mixtures*. It is similar to melting of the ice or the solid state materials in parts because the particles which gain kinetic energy start moving in x,y,z directions with definite pressure and thus the less is the cohesive force more is the pressure exerted by the kinetically moving molecules which strike the walls. But when the molecules move on the fixed track that is noted under the capillary phenomenon within the rigid wall example is Schrodinger equation within the solid wall. Thus, the particles distribution occurs in 2 D and in such cases *the friccohesity is called restricted friccohesity within boundaries.*

Falling Piston Viscometer

Also known as the Norcross viscometer after its inventor, Austin Norcross. The principle of viscosity measurement in this rugged and sensitive industrial device is based on a piston and cylinder assembly. The piston is periodically raised by an air lifting mechanism, drawing the material being measured down through the clearance (gap) between the piston and the wall of the cylinder into the space which is formed below the piston as it is raised. The assembly is then typically held up for a few seconds, then allowed to fall by gravity, expelling the sample out through the same path that it entered, creating a shearing effect on the measured liquid, which makes this viscometer particularly sensitive and good for measuring certain thixotropic liquids. The time of fall is a measure of viscosity, with the clearance between the piston and inside of the cylinder forming the measuring orifice. The viscosity controller measures the time of fall (time-of-fall seconds being the measure of viscosity) and displays the resulting

Fig. 32: Showing the Falling piston Viscometer

viscosity value. The controller can calibrate the time-of-fall value to cup seconds (known as efflux cup), Saybolt universal second (SUS) or centipoise.

Industrial use is popular due to simplicity, repeatability, low maintenance and longevity. This type of measurement is not affected by flow rate or external vibrations. The principle of operation can be adapted for many different conditions, making it ideal for process control environments.

Oscillating Piston Viscometer

Sometimes referred to as electromagnetic viscometer or EMV viscometer, was invented at Cambridge Viscosity (Formally Cambridge Applied Systems) in 1986. The sensor (see figure below) comprises a measurement chamber and magnetically influenced piston. Measurements are taken whereby a sample is first introduced into the thermally controlled measurement chamber where the piston resides. Electronics drive the piston into oscillatory motion within the measurement chamber with a controlled magnetic field. A shear stress is imposed on the liquid (or gas) due to the piston travel and the viscosity is determined by measuring the travel time

Instrumental Chemistry

of the piston. The construction parameters for the annular spacing between the piston and measurement chamber, the strength of the electromagnetic field, and the travel distance of the piston are used to calculate the viscosity according to Newton's Law of Viscosity.

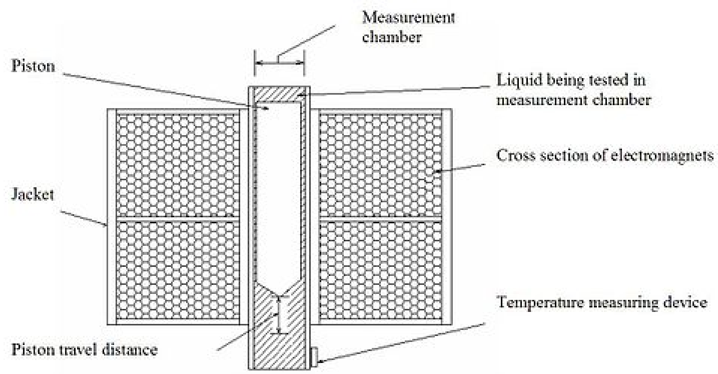


Fig. 33: Oscillating Piston Viscometer

The oscillating piston viscometer technology has been adapted for small sample viscosity and micro-sample viscosity testing in laboratory applications. It has also been adapted to measure high pressure viscosity and high temperature viscosity measurements in both laboratory and process environments. The viscosity sensors have been scaled for a wide range of industrial applications such as small size viscometers for use in compressors and engines, flow-through viscometers for dip coating processes, in-line viscometers for use in refineries, and hundreds of other applications. Improvements in sensitivity from modern electronics, is stimulating a growth in oscillating piston viscometer popularity with academic laboratories exploring gas viscosity.

Vibrational Viscometers

Vibrational viscometers date back to the 1950s Bendix instrument, which is of a class that operates by measuring the damping of an oscillating electromechanical resonator immersed in a fluid whose viscosity is to be determined. The resonator generally oscillates in torsion or transversely (as a cantilever beam or tuning fork). The higher the viscosity, the larger the damping imposed on

the resonator. The resonator's damping may be measured by one of several methods:

1. Measuring the power input necessary to keep the oscillator vibrating at a constant amplitude. The higher the viscosity, the more power is needed to maintain the amplitude of oscillation.
2. Measuring the decay time of the oscillation once the excitation is switched off. The higher the viscosity, the faster the signal decays.
3. Measuring the frequency of the resonator as a function of phase angle between excitation and response waveforms. The higher the viscosity, the larger the frequency change for a given phase change.

The vibrational instrument also suffers from a lack of a defined shear field, which makes it unsuited to measuring the viscosity of a fluid whose flow behaviour is not known before hand.

Vibrating viscometers are rugged industrial systems used to measure viscosity in the process condition. The active part of the sensor is a vibrating rod. The vibration amplitude varies according to the viscosity of the fluid in which the rod is immersed. These viscosity meters are suitable for measuring clogging fluid and high-viscosity fluids, including those with fibers (up to 1,000 Pa•s). Currently, many industries around the world consider these viscometers to be the most efficient system with which to measure the viscosities of a wide range of fluids; by contrast, rotational viscometers require more maintenance, are unable to measure clogging fluid, and require frequent calibration after intensive use. Vibrating viscometers have no moving parts, no weak parts and the sensitive part is very small. Even very basic or acidic fluids can be measured by adding a protective coating such as enamel, or by changing the material of the sensor to a material such as 316L stainless steel.

Rotational Viscometers

Rotational viscometers use the idea that the torque required to turn an object in a fluid is a function of the viscosity of that fluid. They measure the torque required to rotate a disk or bob in a fluid at a known speed.

'Cup and bob' viscometers work by defining the exact volume of a sample which is to be sheared within a test cell; the torque required to achieve a certain rotational speed is measured and plotted. There are two classical geometries in "cup and bob" viscometers, known as either the "Couette" or "Searle" systems - distinguished by whether the cup or bob rotates. The rotating cup is preferred in some cases because it reduces the onset of Taylor vortices, but is more difficult to measure accurately.

'Cone and Plate' viscometers use a cone of very shallow angle in bare contact with a flat plate. With this system the shear rate beneath the plate is constant to a modest degree of precision and deconvolution of a flow curve; a graph of shear stress (torque) against shear rate (angular velocity) yields the viscosity in a straightforward manner.

Electromagnetically Spinning Sphere Viscometer (EMS Viscometer)

The EMS Viscometer measures the viscosity of liquids through observation of the rotation of a sphere which is driven by electromagnetic interaction: Two magnets attached to a rotor

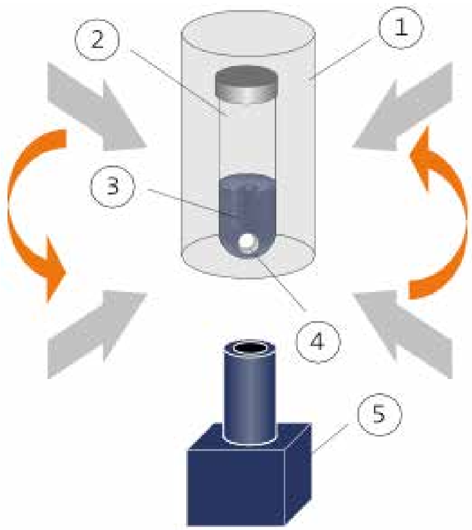


Fig. 34: Measuring Principle of the Electromagnetically Spinning Sphere Viscometer

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create a rotating magnetic field. The sample (3) to be measured is in a small test tube (2). Inside the tube is an aluminium sphere (4). The tube is located in a temperature controlled chamber (1) and set such that the sphere is situated in the centre of the two magnets. The rotating magnetic field induces eddy currents in the sphere. The resulting Lorentz interaction between the magnetic field and these eddy currents generate torque that rotates the sphere. The rotational speed of the sphere depends on the rotational velocity of the magnetic field, the magnitude of the magnetic field and the viscosity of the sample around the sphere. The motion of the sphere is monitored by a video camera (5) located below the cell. The torque applied to the sphere is proportional to the difference in the angular velocity of the magnetic field ΩB and the one of the sphere ΩS. There is thus a linear relationship between (ΩB–ΩS)/ΩS and the viscosity of the liquid.

This new measuring principle was developed by Sakai et al. at the University of Tokyo. The EMS viscometer distinguishes itself from other rotational viscometers by three main characteristics:

- All parts of the viscometer which come in direct contact with the sample are disposable and inexpensive.
- The measurements are performed in a sealed sample vessel.
- The EMS Viscometer requires only very small sample quantities (0.3 mL).

Stabinger Viscometer

By modifying the classic Couette rotational viscometer, an accuracy comparable to that of kinematic viscosity determination is achieved. The internal cylinder in the Stabinger Viscometer is hollow and specifically lighter than the sample, thus floats freely in the sample, centered by centrifugal forces. The formerly inevitable bearing friction is thus fully avoided. The speed and torque measurement is implemented without direct contact by a rotating magnetic field and an eddy current brake. This allows for a previously unprecedented torque resolution of 50 pN•m and an exceedingly large measuring range from 0.2 to 20,000 mPa•s with a single measuring system. A built-in density measurement based on the oscillating U-tube principle allows the determination of kinematic viscosity from the measured dynamic viscosity employing the relation

$$\nu = \frac{\eta}{\rho}$$

The Stabinger Viscometer was presented for the first time by Anton Paar GmbH at the ACHEMA in the year 2000. The measuring principle is named after its inventor Dr. Hans Stabinger.

Bubble Viscometer

Bubble viscometers are used to quickly determine kinematic viscosity of known liquids such as resins and varnishes. The time required for an air bubble to rise is directly proportional to the viscosity of the liquid, so the faster the bubble rises, the lower the viscosity. The Alphabetical Comparison Method uses 4 sets of lettered reference tubes, A5 through Z10, of known viscosity to cover a viscosity range from 0.005 to 1,000 stokes. The Direct Time Method uses a single 3-line times tube for determining the "bubble seconds", which may then be converted to stokes.

Micro-Slit Viscometers

Viscosity measurement using flow through a slit dates back to 1838 when Mr. Jean Louis Marie Poiseuille conducted experiments to characterize the liquid flow through a pipe. He found that a viscous flow through a circular pipe requires pressure to overcome the wall shear stress. That was the birth of Hagen-Poiseuille flow equation. The slit viscometer geometry has flows analogous to the cylindrical pipe but has the additional advantage that no entrance or exit pressure drop corrections are needed. Detailed information regarding the implementation of this principal with modern MEMS and microfluidic science is further explained in a paper by RheoSense, Inc.

Generally, the slit viscosity technology offers the following advantages:

- Measures true (absolute) viscosity for both Newtonian and non-Newtonian fluids
- Enclosed system eliminates air interface and sample evaporation effects
- Measurements can be made using very small sample volumes
- Laminar flow even at high shear rates due to low Reynolds number

- Slit flow simulates real application flow conditions like drug injection or inkjetting.

Miscellaneous viscometer types

Other viscometer types use balls or other objects. Viscometers that can characterize non-Newtonian fluids are usually called *rheometers or plastometers*.

In the I.C.I "Oscar" viscometer, a sealed can of fluid was oscillated torsionally, and by clever measurement techniques it was possible to measure both viscosity and elasticity in the sample.

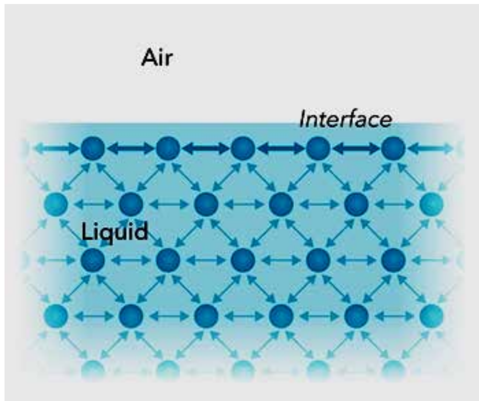
The Marsh funnel viscometer measures viscosity from the time (*efflux time*) it takes a known volume of liquid to flow from the base of a cone through a short tube. This is similar in principle to the flow cups (efflux cups) like the Ford, Zahn and Shell cups which use different shapes to the cone and various nozzle sizes. The measurements can be done according to ISO 2431, ASTM D1200 - 10 or DIN 53411.

12

Measurement of Surface Tension

What is Surface Tension?

Surface tension is a measurement of the cohesive energy present at an interface. The molecules of a liquid attract each other. The interactions of a molecule in the bulk of a liquid are balanced by an equal attractive force in all directions. Molecules on the surface of a liquid experience an imbalance of forces as indicated below.(fig. 35)



How is Surface Tension Measured?

As mentioned above, surface tension can be measure using force tensiometers or optical tensiomters (also known as contact angle meter or

goniometer). Bubble tensiometry can also be used but will not be described below

Basic Physics

Two Definitions: Surface tension, represented by the symbol γ is defined as the force along a line of unit length, where the force is parallel to the surface but perpendicular to the line. One way to picture this is to imagine a flat soap film bounded on one side by a taut thread of length, L. The thread will be pulled toward the interior of the film by a force equal to $2\gamma L$ (the factor of 2 is because the soap film has two sides, hence two surfaces). Surface tension is

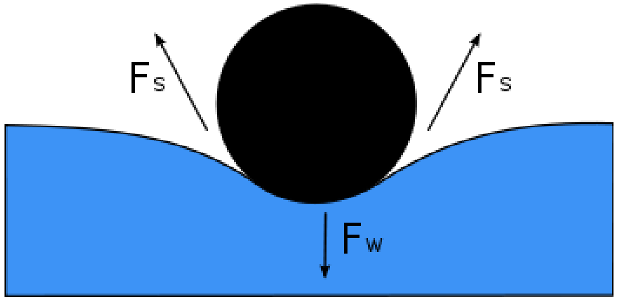


Fig. 36: Diagram shows, in cross-section, a needle floating on the surface of water. Its weight, F_w, depresses the surface, and is balanced by the surface tension forces on either side, F_s, which are each parallel to the water's surface at the points where it contacts the needle. Notice that the horizontal components of the two F_s arrows point in opposite directions, so they cancel each other, but the vertical components point in the same direction and therefore add upto balance F_w.

therefore measured in forces per unit length. Its SI unit is newton per meter but the cgs unit of dyne per cm is also used. One dyn/cm corresponds to 0.001 N/m. An equivalent definition, one that is useful in thermodynamics, is work done per unit area. As such, in order to increase the surface area of a mass of liquid by an amount, δA, a quantity of work, δA, is needed. This work is stored as potential energy. Consequently surface tension can be also measured in SI system as joules per square meter and in the cgs system as ergs per cm^2. Since mechanical systems try to find a state of minimum

potential energy, a free droplet of liquid naturally assumes a spherical shape, which has the minimum surface area for a given volume. The equivalence of measurement of energy per unit area to force per unit length can be proven by dimensional analysis.

Surface Curvature and its Pressure Existing

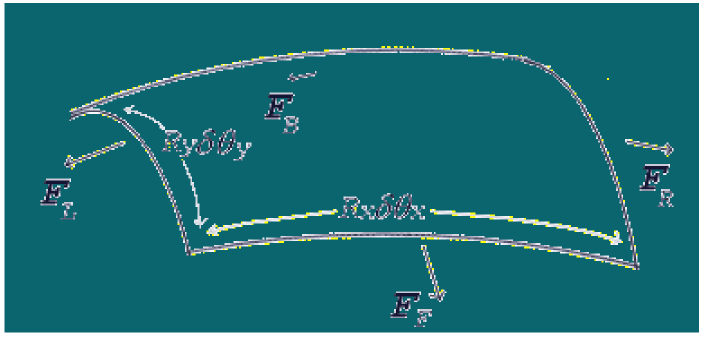


Fig. 37: Surface tension forces acting on a tiny (differential) patch of surface. $\delta\theta_x$ and $\delta\theta_y$ indicate the amount of bend over the dimensions of the patch. Balancing the tension forces with pressure leads to the Young-Laplace equation

If no force acts normal to a tensioned surface, the surface must remain flat. But if the pressure on one side of the surface differs from pressure on the other side, the pressure difference times surface area results in a normal force. In order for the surface tension forces to cancel the force due to pressure, the surface must be curved. The diagram shows how surface curvature of a tiny patch of surface leads to a net component of surface tension forces acting normal to the center of the patch. When all the forces are balanced, the resulting equation is known as the Young–Laplace equation:

$$\Delta p = \gamma\left(\frac{1}{R_x}+\frac{1}{R_y}\right)$$

where:

- Δp is the pressure difference.
- γ is surface tension.
- R_x and R_y are radii of curvature in each of the axes that are parallel to the surface.

The quantity in parentheses on the right hand side is in fact (twice) the mean curvature of the surface (depending on normalisation).

Solutions to this equation determine the shape of water drops, puddles, menisci, soap bubbles, and all other shapes determined by surface tension (such as the shape of the impressions that a water strider's feet make on the surface of a pond).

The table below shows how the internal pressure of a water droplet increases with decreasing radius. For not very small drops the effect is subtle, but the pressure difference becomes enormous when the drop sizes approach the molecular size. (In the limit of a single molecule the concept becomes meaningless.) approach the molecular size. (In the limit of a single molecule the concept becomes meaningless.)

Δp for water drops of different radii at STP

Droplet radius	1 mm	0.1 mm	1 μm	10 nm
Δp (atm)	0.0014	0.0144	1.436	143.6

Liquid Surface

To find the shape of the minimal surface bounded by some arbitrary shaped frame using strictly mathematical means can be a daunting task. Yet by fashioning the frame out of wire and dipping it in soap-solution, a locally minimal surface will appear in the resulting soap-film within seconds. The reason for this is that the pressure difference across a fluid interface is proportional to the mean curvature, as seen in the Young-Laplace equation. For an open

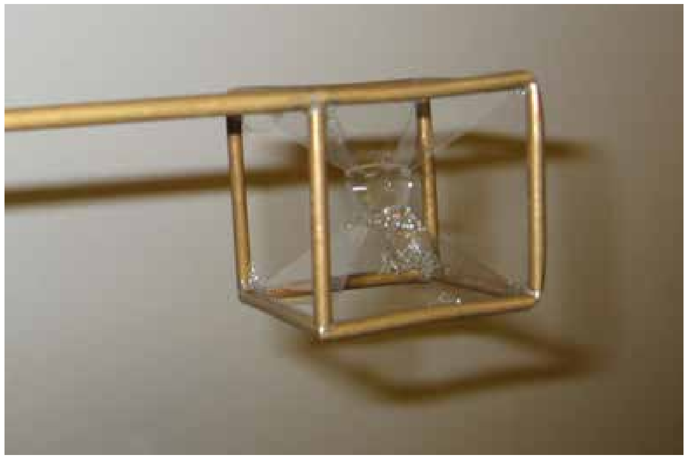


Fig. 38: Showing the area of Minimal surface

soap film, the pressure difference is zero, hence the mean curvature is zero, and minimal surfaces have the property of zero mean curvature.

Contact Angles

The surface of any liquid is an interface between that liquid and some other medium. The top surface of a pond, for example, is an interface between the pond water and the air. Surface tension, then, is not a property of the liquid alone, but a property of the liquid's interface with another medium. If a liquid is in a container, then besides the liquid/air interface at its top surface, there is also an interface between the liquid and the walls of the container. The surface tension between the liquid and air is usually different (greater than) its surface tension with the walls of a container. And where the two surfaces meet, their geometry must be such that all forces balance.

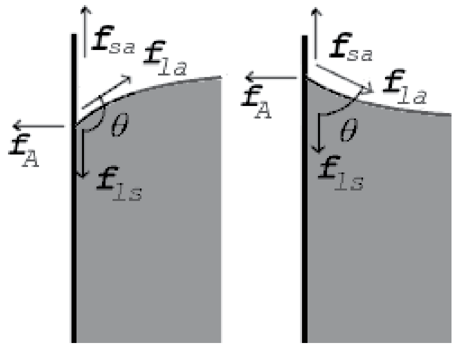


Fig. 39: Forces at contact point shown for contact angle greater than 90° (left) and less than 90° (right)

Where the two surfaces meet, they form a contact angle, θ, which is the angle the tangent to the surface makes with the solid surface. The diagram to the right shows two examples. Tension forces are shown for the liquid-air interface, the liquid-solid interface, and the solid-air interface. The example on the left is where the difference between the liquid-solid and solid-air surface tension, $\eta_s - \eta_{sa}$, is less than the liquid-air surface tension, η_a, but is nevertheless positive, that is:

$$\gamma_{la} > \gamma_{ls} - \gamma_{sa} > 0$$

Instrumental Chemistry

In the diagram, both the vertical and horizontal forces must cancel exactly at the contact point, known as equilibrium. The horizontal component of f_{la} is canceled by the adhesive force, f_{la}.

$$f_{\mathrm{A}} = f_{\mathrm{la}} \sin\theta$$

The more telling balance of forces, though, is in the vertical direction. The vertical component of must exactly cancel the force, f_{la}.

$$f_{\mathrm{ls}} - f_{\mathrm{sa}} = -f_{\mathrm{la}} \cos\theta$$

Liquid	Solid	Contact angle
water	soda-lime glass lead glass fused quartz	0°
ethanol		
diethyl ether		
carbon tetrachloride		
glycerol		
acetic acid		
water	paraffin wax	107°
	silver	90°
methyl iodide	soda-lime glass	29°
	lead glass	30°
	fused quartz	33°
mercury	soda-lime glass	140°

Some liquid-solid contact angles

Since the forces are in direct proportion to their respective surface tensions, we also have:

$$\gamma_{\mathrm{ls}} - \gamma_{\mathrm{sa}} = -\gamma_{\mathrm{la}} \cos\theta$$

where

- η_s is the liquid-solid surface tension,
- η_a is the liquid-air surface tension,
- η_{sa} is the solid-air surface tension,
- θ is the contact angle, where a concave meniscus has contact angle less than 90° and a convex meniscus has contact angle of greater than 90°.

This means that although the difference between the liquid-solid and solid-air surface tension, $\eta_s - \eta_{sa}$, is difficult to measure directly, it can be inferred from the liquid-air surface tension, η_a,

and the equilibrium contact angle, θ, which is a function of the easily measurable advancing and receding contact angles (see main article contact angle).

This same relationship exists in the diagram on the right. But in this case we see that because the contact angle is less than 90°, the liquid-solid/solid-air surface tension difference must be negative:

$$\gamma_{\mathrm{la}} > 0 > \gamma_{\mathrm{ls}} - \gamma_{\mathrm{sa}}$$

Special Contact Angles

Observe that in the special case of a water-silver interface where the contact angle is equal to 90°, the liquid-solid/solid-air surface tension difference is exactly zero. Another special case is where the contact angle is exactly 180°. Water with specially prepared Teflon approaches this. Contact angle of 180° occurs when the liquid-solid surface tension is exactly equal to the liquid-air surface tension.

$$\gamma_{\mathrm{la}} = \gamma_{\mathrm{ls}} - \gamma_{\mathrm{sa}} > 0 \qquad \theta = 180^\circ$$

Methods of Measurement

Because surface tension manifests itself in various effects, it offers a number of paths to its measurement. Which method is

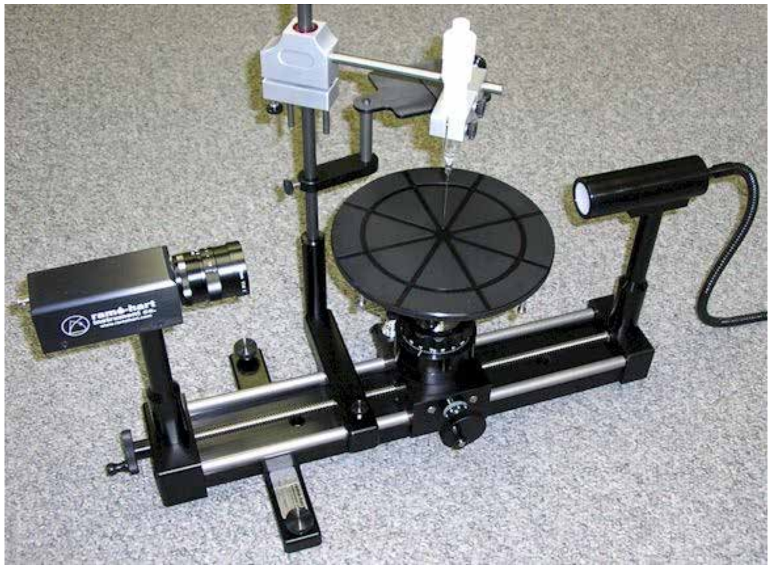


Fig. 40: Surface tension can be measured using the pendant drop method on a goniometer

optimal depends upon the nature of the liquid being measured, the conditions under which its tension is to be measured, and the stability of its surface when it is deformed.

- **Du Noüy Ring method**: The traditional method used to measure surface or interfacial tension. Wetting properties of the surface or interface have little influence on this measuring technique. Maximum pull exerted on the ring by the surface is measured.
- **Du Noüy-Padday method**: A minimized version of Du Noüy method uses a small diameter metal needle instead of a ring, in combination with a high sensitivity microbalance to record maximum pull. The advantage of this method is that very small sample volumes (down to few tens of microliters) can be measured with very high precision, without the need to correct for buoyancy (for a needle or rather, rod, with proper geometry). Further, the measurement can be performed very quickly, minimally in about 20 seconds. First commercial multichannel tensiometers [CMCeeker] were recently built based on this principle.
- **Wilhelmy plate method**: A universal method especially suited to check surface tension over long time intervals. A vertical plate of known perimeter is attached to a balance, and the force due to wetting is measured.
- **Spinning drop method**: This technique is ideal for measuring low interfacial tensions. The diameter of a drop within a heavy phase is measured while both are rotated.
- **Pendant drop method**: Surface and interfacial tension can be measured by this technique, even at elevated temperatures and pressures. Geometry of a drop is analyzed optically. For details, see Drop.
- **Bubble pressure method (Jaeger's method)**: A measurement technique for determining surface tension at short surface ages. Maximum pressure of each bubble is measured.
- **Drop volume method**: A method for determining interfacial tension as a function of interface age. Liquid of one density is pumped into a second liquid of a different density and time between drops produced is measured.

- **Capillary rise method**: The end of a capillary is immersed into the solution. The height at which the solution reaches inside the capillary is related to the surface tension by the equation discussed below.
- **Stalagmometric method**: A method of weighting and reading a drop of liquid.
- **Sessile drop method**: A method for determining surface tension and density by placing a drop on a substrate and measuring the contact angle (see Sessile drop technique).
- **Vibrational frequency of levitated drops**: The natural frequency of vibrational oscillations of magnetically levitated drops has been used to measure the surface tension of superfluid. This value is estimated to be 0.375 dyn/cm at T = 0 K.

Effects— Liquid in a Vertical Tube

An old style mercury barometer consists of a vertical glass tube about 1 cm in diameter partially filled with mercury, and with a vacuum (called Torricelli's vacuum) in the unfilled volume (see diagram to the right). Notice that the mercury level at the center of the tube is higher than at the edges, making the upper surface of the mercury dome-

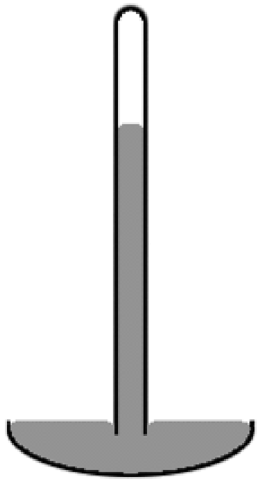


Fig. 41: Diagram of a mercury barometer

shaped. The center of mass of the entire column of mercury would be slightly lower if the top surface of the mercury were flat over the entire crossection of the tube. But the dome-shaped top gives slightly less surface area to the entire mass of mercury. Again the two effects combine to minimize the total potential energy. Such a surface shape is known as a convex meniscus. The reason we consider the surface area of the entire mass of mercury, including the part of the surface that is in contact with the glass, is because mercury does not adhere at all to glass. So the surface tension of the mercury acts over its entire surface area, including where it is in contact with the glass. If instead of glass, the tube were made out of copper, the situation would be very different. Mercury aggressively adheres to copper. So in a copper tube, the level of mercury at the center of the tube will be lower than at the edges (that is, it would be a concave meniscus). In a situation where the liquid adheres to the walls of its container, we consider the part of the fluid's surface area that is in contact with the container to have negative surface tension. The fluid then works to maximize the contact surface area. So in this case increasing the area in contact with the container decreases rather than increases the potential energy. That decrease is enough to compensate for the increased potential energy associated with lifting the fluid near the walls of the container.

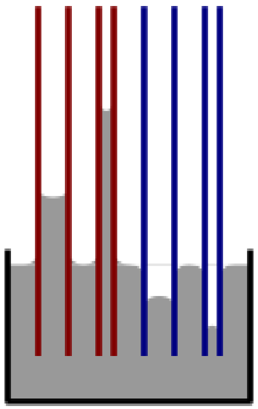


Fig. 42: Illustration of capillary rise and fall. Red=contact angle less than 90°; blue=contact angle greater than 90°

If a tube is sufficiently narrow and the liquid adhesion to its walls

is sufficiently strong, surface tension can draw liquid up the tube in a phenomenon known as capillary action. The height the column is lifted to is given by:

$$h = \frac{2\gamma_{\mathrm{la}}\cos\theta}{\rho g r}$$

where

- h is the height the liquid is lifted,
- ηa is the liquid-air surface tension,
- ρ is the density of the liquid,
- r is the radius of the capillary,
- ϑ is the acceleration due to gravity,
- θ is the angle of contact described above. If θ is greater than 90°, as with mercury in a glass container, the liquid will be depressed rather than lifted.

Puddles on a Surface

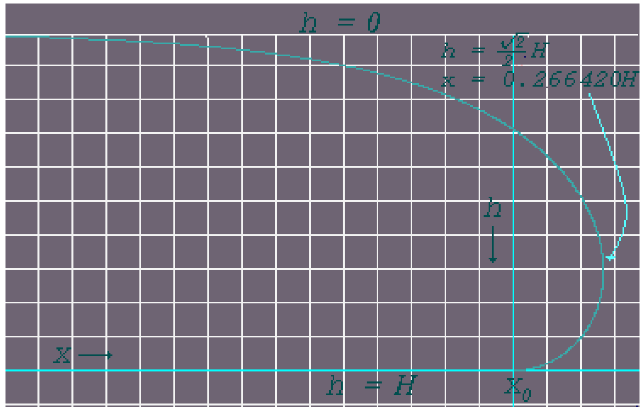


Fig. 43: Profile curve of the edge of a puddle where the contact angle is 180°. The curve is given by the formula:

$$x - x_0 = \frac{1}{2}H\cosh^{-1}\left(\frac{H}{h}\right) - H\sqrt{1-\frac{h^2}{H^2}}$$

where

$$H = 2\sqrt{\frac{\gamma}{g\rho}}$$

Pouring mercury onto a horizontal flat sheet of glass results in a puddle that has a perceptible thickness. The puddle will spread out

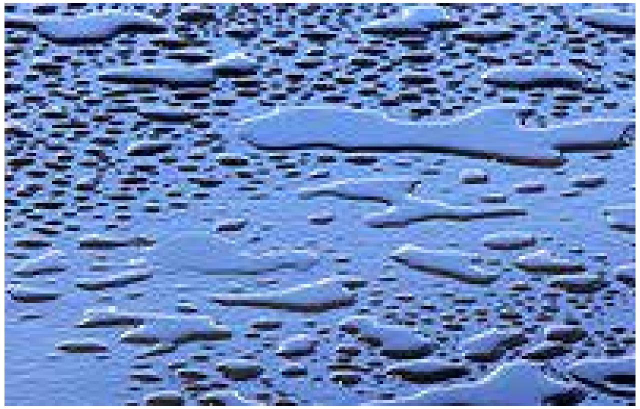


Fig. 44: Small puddles of water on a smooth clean surface have perceptible thickness

only to the point where it is a little under half a centimeter thick, and no thinner. Again this is due to the action of mercury's strong surface tension. The liquid mass flattens out because that brings as much of the mercury to as low a level as possible, but the surface tension, at the same time, is acting to reduce the total surface area. The result is the compromise of a puddle of a nearly fixed thickness.

The same surface tension demonstration can be done with water, lime water or even saline, but only on a surface made of a substance that the water does not adhere to. Wax is such a substance. Water poured onto a smooth, flat, horizontal wax surface, say a waxed sheet of glass, will behave similarly to the mercury poured onto glass.

The thickness of a puddle of liquid on a surface whose contact angle is 180° is given by:

$$h = 2\sqrt{\frac{\gamma}{g\rho}}$$

where

- h is the depth of the puddle in centimeters or meters.
- γ is the surface tension of the liquid in dynes per centimeter or newtons per meter.
- ϑ is the acceleration due to gravity and is equal to 980 cm/s2 or 9.8 m/s2
- ρ is the density of the liquid in grams per cubic centimeter or kilograms per cubic meter

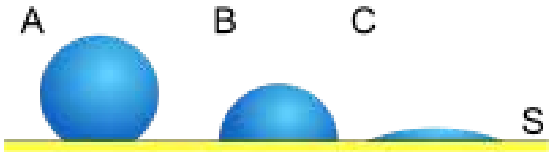


Fig. 45: Illustration of how lower contact angle leads to reduction of puddle depth

In reality, the thicknesses of the puddles will be slightly less than what is predicted by the above formula because very few surfaces have a contact angle of 180° with any liquid. When the contact angle is less than 180°, the thickness is given by:

$$h = \sqrt{\frac{2\gamma_{\mathrm{la}}\,(1-\cos\theta)}{g\rho}}.$$

For mercury on glass, γ_{Hg} = 487 dyn/cm, ρ_{Hg} = 13.5 g/cm^3 and θ = 140°, which gives h_{Hg} = 0.36 cm. For water on paraffin at 25 °C, γ = 72 dyn/cm, ρ = 1.0 g/cm^3, and θ = 107° which gives h_{H2O} = 0.44 cm.

The formula also predicts that when the contact angle is 0°, the liquid will spread out into a micro-thin layer over the surface. Such a surface is said to be fully wettable by the liquid.

The Breakup of Streams into Drops

In day-to-day life we all observe that a stream of water emerging from a faucet will break up into droplets, no matter how smoothly the stream is emitted from the faucet. This is due to a phenomenon called the Plateau–Rayleigh instability,[6] which is entirely a consequence of the effects of surface tension.

The explanation of this instability begins with the existence of tiny perturbations in the stream. These are always present, no matter how smooth the stream is. If the perturbations are resolved into sinusoidal components, we find that some components grow with time while others decay with time. Among those that grow with time, some grow at faster rates than others. Whether a component decays or grows, and how fast it grows is entirely a function of its wave number (a measure of how many peaks and troughs per centimeter) and the radii of the original cylindrical stream.

Thermodynamics

As stated above, the mechanical work needed to increase a

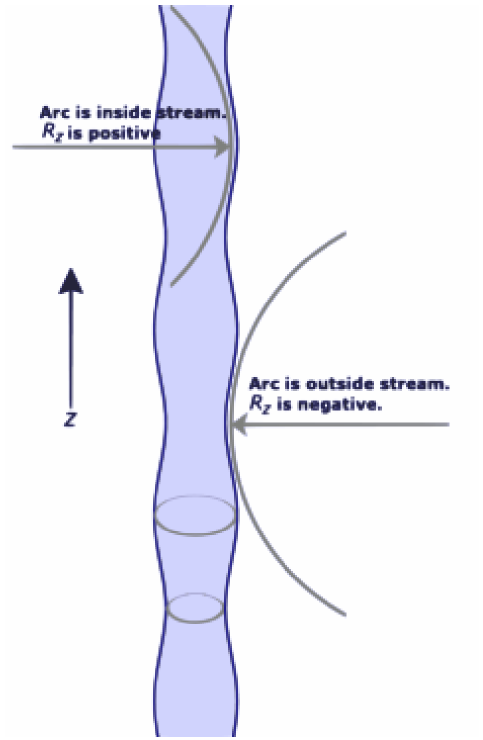


Fig. 46: Intermediate stage of a jet breaking into drops. Radii of curvature in the axial direction are shown. Equation for the radius of the stream is $R(z)=R_0+A_k\cos(kz)$, where R_0 is the radius of the unperturbed stream is $R(z)=R_0+A_k\cos(kz)$, the amplitude of the perturbation, z is distance along the axis of the stream, A^k and is the wave number

surface is . Hence at constant temperature and pressure, surface tension equals Gibbs free energy per surface area:

$$\gamma = \left(\frac{\partial G}{\partial A}\right)_{T,P,n}$$

where G is Gibbs free energy and A is the area.

Thermodynamics requires that all spontaneous changes of state are accompanied by a decrease in Gibbs free energy.

From this it is easy to understand why decreasing the surface area of a mass of liquid is always spontaneous ($\Delta G < 0$), provided it is not coupled to any other energy changes. It follows that in order to increase surface area, a certain amount of energy must be added.

Gibbs free energy is defined by the equation, $G = H - TS$, where is enthalpy and is entropy. Based upon this and the fact that surface tension is Gibbs free energy per unit area, it is possible to obtain the following expression for entropy per unit area:

$$\left(\frac{\partial\gamma}{\partial T}\right)_{A,P} = -S^A$$

Kelvin's Equation for surfaces arises by rearranging the previous equations. It states that surface enthalpy or surface energy (different from surface free energy) depends both on surface tension and its derivative with temperature at constant pressure by the relationship.

$$H^A = \gamma - T\left(\frac{\partial\gamma}{\partial T}\right)_P$$

Thermodynamics of Soap Bubbles

The pressure inside an ideal (one surface) soap bubble can be derived from thermodynamic free energy considerations. At constant temperature and particle number, $dT = dN = 0$, the differential Helmholtz energy is given by

$$dF = -PdV + \gamma dA$$

where P is the difference in pressure inside and outside of the bubble, and γ is the surface tension. In equilibrium, $dF = 0$, and so,

$$PdV = \gamma dA\,.$$

For a spherical bubble, the volume and surface area are given simply by

$$V = \frac{4}{3}\pi R^3 \rightarrow dV \approx 4\pi R^2 dR\,,$$

and

$$A = 4\pi R^2 \rightarrow dA \approx 8\pi R dR.$$

Substituting these relations into the previous expression, we find

$$P = \frac{2}{R}\gamma\,,$$

which is equivalent to the Young–Laplace equation when $R_x = R_y$. For real soap bubbles, the pressure is doubled due to the presence of two interfaces, one inside and one outside.

Instrumental Chemistry

Influence of Temperature

Surface tension is dependent on temperature. For that reason, when a value is given for the surface tension of an interface, temperature must be explicitly stated. The general trend is that

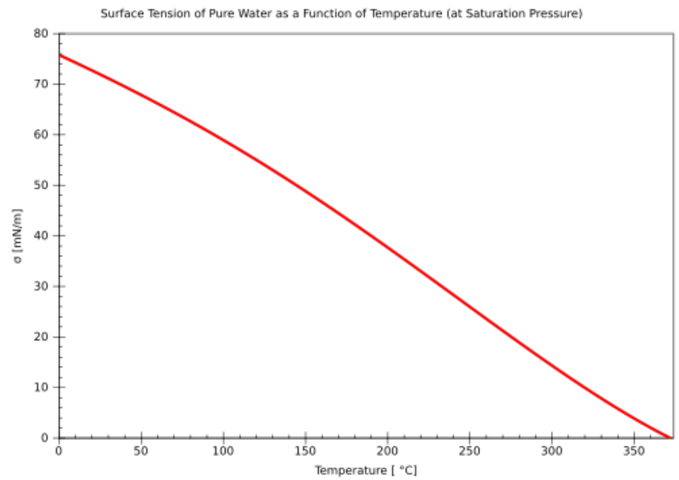


Fig. 47: Temperature dependence of the surface tension of pure water

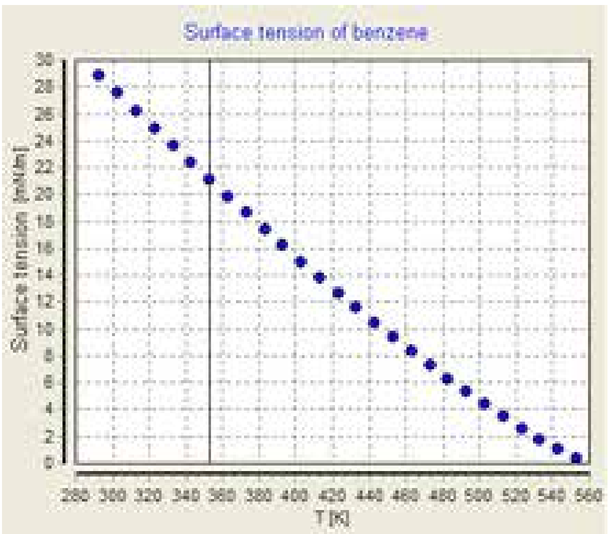


Fig. 48: Temperature dependency of the surface tension of benzene

surface tension decreases with the increase of temperature, reaching a value of 0 at the critical temperature. For further details see Eötvös rule. There are only empirical equations to relate surface tension and temperature:

- Eötvös:

$$\gamma V^{2/3} = k(T_C - T)$$

Here V is the molar volume of a substance, *TC is the critical temperature and k is a constant valid for almost all substances. A typical value is k = 2.1 x* 10^{-7} *[J* K^{-1} *mol*$^{-2/3}$*]. For water one can further use V = 18 ml/mol and* $T_C = 374$*°C.*

A variant on Eötvös is described by Ramay and Shields:

$$\gamma V^{2/3} = k\,(T_C - T - 6)$$

where the temperature offset of 6 kelvins provides the formula with a better fit to reality at lower temperatures.

- Guggenheim-Katayama

$$\gamma = \gamma^o \left(1 - \frac{T}{T_C}\right)^n$$

γ^0 is a constant for each liquid and n is an empirical factor, whose value is 11/9 for organic liquids. This equation was also proposed by van der Waals, who further proposed that γ^0 could be given by the expression, $K_2 T_c^{\frac{1}{3}} P_c^{\frac{2}{3}}$, where K_2 is a universal constant for all liquids, and is the critical pressure of the liquid (although later experiments found to vary to some degree from one liquid to another).

Both Guggenheim-Katayama and Eötvös take into account the fact that surface tension reaches 0 at the critical temperature, whereas Ramay and Shields fails to match reality at this endpoint.

Influence of Solute Concentration

Solutes can have different effects on surface tension depending on their structure:

- Little or no effect, for example sugar
- Increase surface tension, inorganic salts
- Decrease surface tension progressively, alcohols
- Decrease surface tension and, once a minimum is reached, no more effect: surfactants

What complicates the effect is that a solute can exist in a different concentration at the surface of a solvent than in its bulk. This difference varies from one solute/solvent combination to another.

$$\Gamma = -\frac{1}{RT}\left(\frac{\partial\gamma}{\partial \ln C}\right)_{T,P}$$

Gibbs isotherm states that:

- τ is known as surface concentration, it represents excess of solute per unit area of the surface over what would be present if the bulk concentration prevailed all the way to the surface. It has units of mol/m^2
- C is the concentration of the substance in the bulk solution.
- R is the gas constant and the temperature

Certain assumptions are taken in its deduction, therefore Gibbs isotherm can only be applied to ideal (very dilute) solutions with two components.

Influence of Particle Size on Vapor Pressure

The Clausius–Clapeyron relation leads to another equation also attributed to Kelvin, as the Kelvin equation. It explains why, because of surface tension, the vapor pressure for small droplets of liquid in suspension is greater than standard vapor pressure of that same liquid when the interface is flat. That is to say that when a liquid is forming small droplets, the equilibrium concentration of its vapor in its surroundings is greater. This arises because the pressure inside the droplet is greater than outside.

$$P_v^{fog} = P_v^o e^{\frac{V2\gamma}{RTr_k}}$$

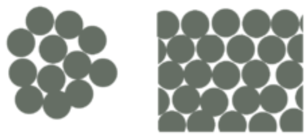


Fig. 49: Molecules on the surface of a tiny droplet (left) have, on average, fewer neighbors than those on a flat surface (right). Hence they are bound more weakly to the droplet than are flat-surface molecules.

- P^o_v is the standard vapor pressure for that liquid at that temperature and pressure.

- V is the molar volume.
- R is the gas constant

R_k is the Kelvin radius, the radius of the droplets.

The effect explains supersaturation of vapors. In the absence of nucleation sites, tiny droplets must form before they can evolve into larger droplets. This requires a vapor pressure many times the vapor pressure at the phase transition point.

This equation is also used in catalyst chemistry to assess mesoporosity for solids

The effect can be viewed in terms of the average number of molecular neighbors of surface molecules (see diagram).

The table shows some calculated values of this effect for water at different drop sizes:

***P/P$_0$* for water drops of different radii at STP**				
Droplet radius (nm)	1000	100	10	1
P/P$_0$	1.001	1.011	1.114	2.95

The effect becomes clear for very small drop sizes, as a drop of 1 nm radius has about 100 molecules inside, which is a quantity small enough to require a quantum mechanics analysis.

Surface tension of various liquids in dyn/cm against air Mixture compositions denoted "%" are by mass dyn/cm is equivalent to the SI units of mN/m (millinewton per meter)

Liquid	**Temperature °C**	**Surface tension, γ**
Acetic acid	20	27.60
Acetic acid (40.1%) + Water	30	40.68
Acetic acid (10.0%) + Water	30	54.56
Acetone	20	23.70
Diethyl ether	20	17.00
Ethanol	20	22.27
Ethanol (40%) + Water	25	29.63
Ethanol (11.1%) + Water	25	46.03
Glycerol	20	63.00
n-Hexane	20	18.40

Hydrochloric acid 17.7M aqueous solution	20	65.95
Isopropanol	20	21.70
Liquid helium II	-273	0.37
Liquid nitrogen	-196	8.85
Mercury	15	487.00
Methanol	20	22.60
n-Octane	20	21.80
Sodium chloride 6.0M aqueous solution	20	82.55
Sucrose (55%) + water	20	76.45
Water	0	75.64
Water	25	71.97
Water	50	67.91
Water	100	58.85
Toluene	25	27.73

Sessile Drop Technique

The Sessile Drop Technique is a method used for the characterization of solid surface energies, and in some cases, aspects of liquid surface energies. The main premise of the method is that by placing a droplet of liquid with a known surface energy, the shape of the drop, specifically the contact angle, and the known surface energy of the liquid are the parameters which can be used to

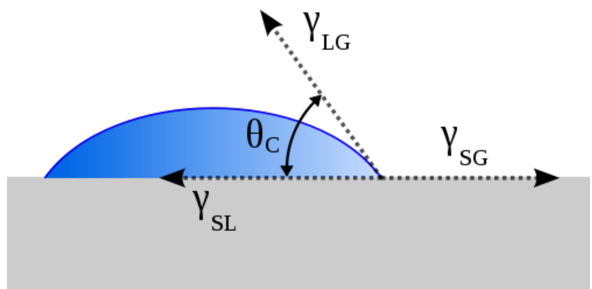


Fig. 50: An illustration of the sessile drop technique with a liquid droplet partially wetting a solid substrate. θ_c is the contact angle, and γ_{SG}, γ_{LG}, γ_{SL} represent the solid-gas, gas-liquid, and liquid-solid interfaces, respectively.

calculate the surface energy of the solid sample. The liquid used for such experiments is referred to as the probe liquid, and the use of several different probe liquids is required.

Probe Liquid

The surface energy is measured in units of Joules per area, which is equivalent in the case of liquids to surface tension, measured in newtons per meter. The overall surface tension/energy of a liquid can be acquired through various methods using a tensiometer or using the pendent drop technique and Maximum bubble pressure method.The interface tension at the interface of the probe liquid and the solid surface can additionally be viewed as being the result of different types of intermolecular forces. As such, surface energies can be subdivided according to the various interactions that cause them, such as the surface energy due to dispersive (van der Waals) forces, hydrogen bonding, polar interactions, acid/base interactions, etc. It is often useful for the sessile drop technique to use liquids that are known to be incapable of some of those interactions (see table 1). For example, the surface tension of all straight alkanes is said to be entirely dispersive, and all of the other components are zero. This is algebraically useful, as it eliminates a variable in certain cases, and makes these liquids essential testing materials. The overall surface energy, both for a solid and a liquid, is assumed traditionally to simply be the sum of the components considered. For example, the equation describing the subdivision of surface energy into the contributions of dispersive interactions and polar interactions would be:

$$\sigma_S = \sigma_S^D + \sigma_S^P$$

$$\sigma_L = \sigma_L^D + \sigma_L^P$$

Where σ_S is the total surface energy of the solid, σ_S^D and σ_S^P are respectively the dispersive and polar components of the solid surface energy, σ_L is the total surface tension/surface energy of the liquid, and σ_L^D and σ_L^D are respectively the dispersive and polar components of the surface tension. In addition to the tensiometer and pendant drop techniques, the sessile drop technique can be used in some cases to separate the known total surface energy of a liquid into its components. This is done by reversing the above idea with the introduction of a reference solid surface that is assumed to be incapable of polar interactions, such as Polytetrafluoroethylene (PTFE).

Instrumental Chemistry

Contact Angle

The contact angle is defined as the angle made by the intersection of the liquid/solid interface and the liquid/air interface. It can be alternately described as the angle between solid sample's surface and the tangent of the droplet's ovate shape at the edge of the droplet. A high contact angle indicates a low solid surface energy or chemical affinity. This is also referred to as a low degree of wetting. A low contact angle indicates a high solid surface energy or chemical affinity, and a high or sometimes complete degree of wetting. For example, a contact angle of zero degrees will occur when the droplet has turned into a flat puddle; this is called complete wetting.

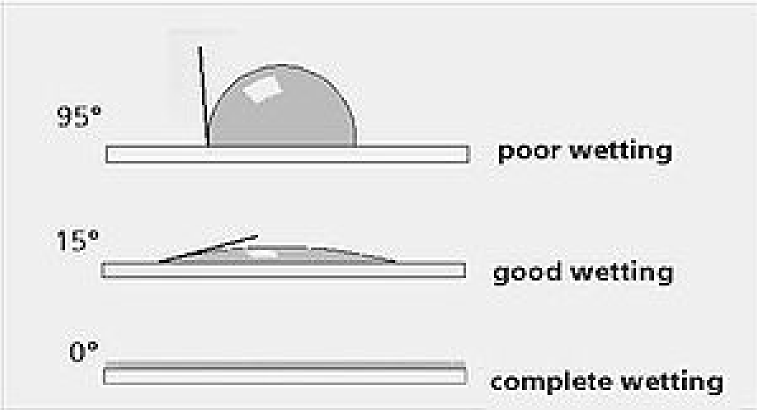


Fig. 51: A sketch of three degrees of wetting and the corresponding contact angles

Measuring Contact Angle

Goniometer Method

The simplest way of measuring the contact angle is with a goniometer, which allows the user to measure the contact angle visually. The droplet is deposited by a syringe pointed vertically down onto the sample surface, and a high resolution camera captures the image, which can then be analyzed either by eye (with a protractor) or using image analysis software. The size of the droplet can be increased gradually so that it grows proportionally, and the contact angle remains congruent. By taking pictures incrementally as the droplet grows, the user can acquire a set of data to get a good average.

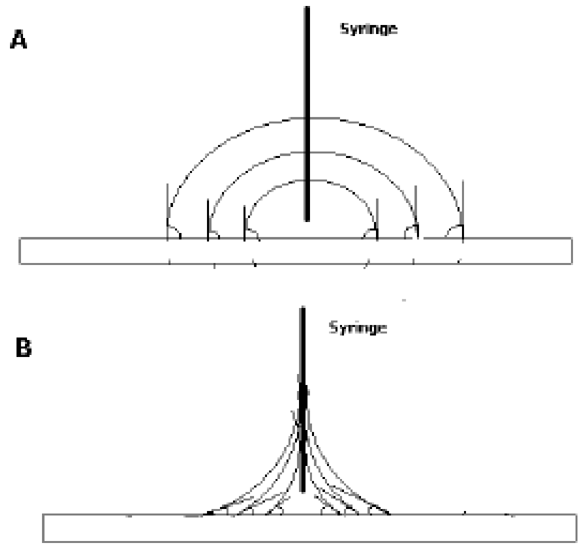


Fig. 52: Sketch of the contact angle, as seen by a goniometer. In the top picture, the volume of the drop is being increased, and in the bottom it is being decreased. Each angle is measure of the same contact angle

If necessary, the receding contact angle can also be measured by depositing a droplet via syringe and recording images of the droplet being gradually sucked back up.

Advantages and Disadvantages

The advantage of this method, aside from its relatively straightforward nature, is the fact that with a large enough solid surface, multiple droplets can be deposited in various locations on the sample to determine heterogeneity. The reproducibility of particular values of the contact angle will reflect the heterogeneity of the surface's energy properties. Conversely, the disadvantage is that if the sample is only large enough for one droplet, then it will be difficult to determine heterogeneity, or consequently to assume homogeneity. This is particularly true because conventional, commercially available goniometers do not swivel the camera/backlight set up relative to the stage, and thus can only show the contact angle at two points: the right and the left edge of the droplet. In addition to this, this measurement is hampered by its inherent subjectivity, as the placement of the lines is determined either by the user looking at the pictures or by the image analysis software's definition of the lines.

Instrumental Chemistry

Wilhelmy Method

An alternative method for measuring the contact angle is the Wilhelmy method, which employs a sensitive force meter of some sort to measure a force that can be translated into a value of the contact angle. In this method, a small plate-shaped sample of the solid in question, attached to the arm of a force meter, is vertically dipped into a pool of the probe liquid (in actuality, the design of a stationary force meter would have the liquid being brought up, rather than the sample being brought down), and the force exerted on the sample by the liquid is measured by the force meter. This force is related to the contact angle by the following equation:

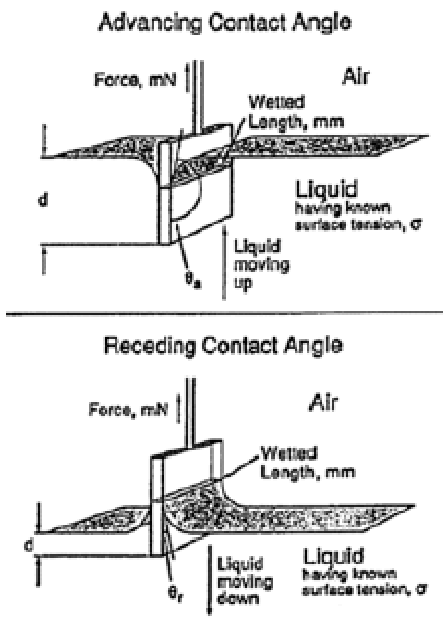


Fig. 53: The Wilhelmy method for measuring contact angle. In the top picture a plate of the solid surface is lowered into a submerging liquid. The liquid pushes up on the solid sample with force due to the buoyancy and the surface tension, and these forces are measured by instruments attached to the arm above the sample, and depend on the length d, surface tension σ, and wetted length I (the perimeter of the sample along the line of contact of the air, liquid, and solid). In the bottom picture the sample is being raised and the liquid exerts a downward force

$$\cos\theta = (F - Fb)/I\sigma$$

Where F is the total force measured by the force meter, Fb is the force of buoyancy due to the solid sample displacing the liquid, I is the wetted length, and sigma is the known surface tension of the liquid.

Advantages and Disadvantages

The advantage of this method is that it is fairly objective and the measurement yields data which is inherently averaged over the wetted length. Although this does not help determine heterogeneity, it does automatically give a more accurate average value. Its disadvantages, aside from being more complicated than the goniometer method, include the fact that sample of an appropriate size must be produced with a uniform cross section in the submersion direction, and the wetted length must be measured with some precision. In addition, this method is only appropriate if both sides of the sample are identical, otherwise the measured data will be a result of two completely different interactions.

Strictly speaking, this is not a sessile drop technique, as we are using a small submerging pool, rather than a droplet. However, the calculations described in the following sections, which were derived for the relation of the sessile drop contact angle to the surface energy, apply just as well.

Determining Surface Energy

While surface energy is conventionally defined as the work required to build a unit of area of a given surface, when it comes to its measurement by the sessile drop technique, the surface energy is not quite as well defined. The values obtained through the sessile drop technique depend not only on the solid sample in question, but equally on the properties of the probe liquid being used, as well as the particular theory relating the parameters mathematically to one another.

There are numerous such theories developed by various researchers. These methods differ in several regards, such as derivation and convention, but most importantly they differ in the number of components or parameters which they are equipped to analyze. The simpler methods containing fewer components simplify the system

Instrumental Chemistry

by lumping surface energy into one number, while more rigorous methods with more components are derived to distinguish between various components of the surface energy. Again, the total surface energy of solids and liquids depends on different types of molecular interactions, such as dispersive (van der Waals), polar, and acid/base interactions, and is considered to be the sum of these independent components. Some theories account for more of these phenomena than do other theories. These distinctions are to be considered when deciding which method is appropriate for the experiment at hand. The following are a few commonly used such theories.

One Component Theories

The Zisman Theory

The Zisman theory is the simplest commonly used theory, as it is a one component theory, and is best used for non-polar surfaces. This means that polymer surfaces that have been subjected to heat treatment, corona treatment, plasma cleaning, or polymers that contain heteroatoms do not lend themselves to this particular theory, as they tend to be at least somewhat polar. The Zisman theory also tends to be more useful in practice for surfaces with lower energies.

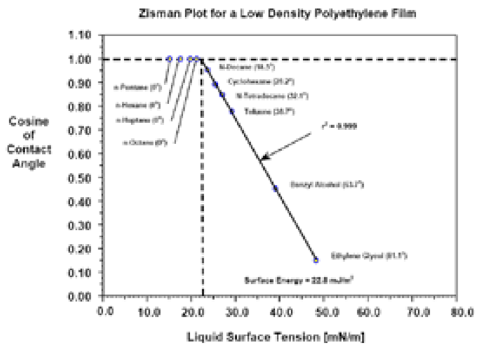


Fig. 54: The Zisman plot for the surface energy of LDPE. Each plot point reflects the contact angle with a specified probe liquid. The line coefficient r^2=.999 indicates a high degree of confidence.

The Zisman theory simply defines the surface energy as being equal to the surface energy of the highest surface energy liquid that wets the solid completely. That is to say, the droplet will disperse as much as possible, i.e. completely wetting the surface, for this liquid and any liquids with lower surface energies, but not for liquids with higher surface energies. Since this probe liquid could hypothetically be any liquid, including an imaginary liquid, the best way to determine the surface energy by the Zisman method is to acquire data points of contact angles for several probe liquids on the solid surface in question, and then plot the cosine of that angle against the known surface energy of the probe liquid. By constructing the Zisman plot, one can extrapolate the highest liquid surface energy, real or hypothetical, that would result in complete wetting of the sample with a contact angle of zero degrees.

Accuracy/Precision

The line coefficient (Fig. 54) suggests that this is a fairly accurate result, however this is only the case for the pairing of that particular solid with those particular liquids. In other cases, the fit may not be so great (such is the case if we replace polyethylene with poly(methyl methacrylate), wherein the line coefficient of the plot results using the same list of liquids would be significantly lower). This shortcoming is a result of the fact that the Zisman theory treats the surface energy as one single parameter, rather than accounting for the fact that, for example, polar interactions are much stronger than dispersive ones, and thus the degree to which one is happening versus the other greatly affects the necessary calculations. As such, it is a simple but not particularly robust theory. Since the premise of this procedure is to determine the hypothetical properties of a liquid, the precision of the result depends on the precision to which the surface energy values of the probe liquids are known.

Two Component Theories

The Owens/Wendt Theory

The Owens/Wendt theory (after C. J. van Oss and John F. Wendt) divides the surface energy into two components: surface energy due to dispersive interactions and surface energy due to polar interactions. This theory is derived from the combination of Young's relation, which relates the contact angle to the surface energies of the solid and liquid and to the interface tension, and Good's equation (after R. J. Good), which relates the interface tension to the polar and dispersive components of the surface energy. The resulting principle

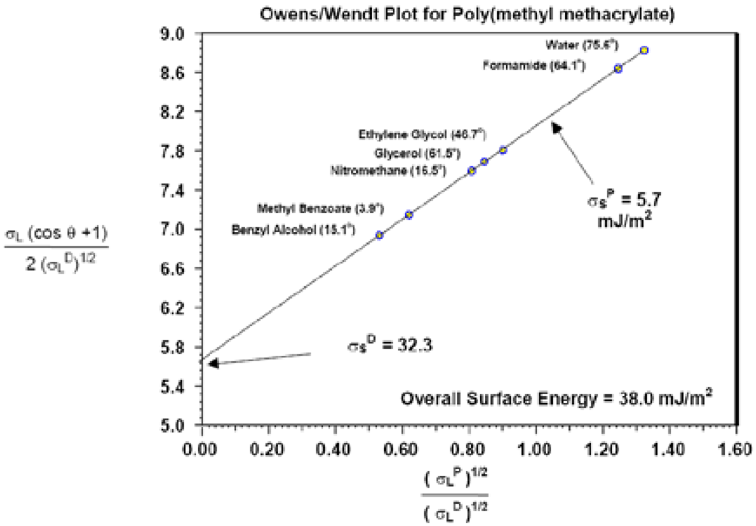


Fig. 55: The Owens-Wendt plot for the surface energy of Poly(Methyl Methacrylate), with each data point reflecting the interaction of the solid with specified liquid. In this case, a high degree of confidence was indicated by a line coefficient of r^2=.998

equation is:

$$\frac{\sigma_L\ (\cos\theta+1)}{2\sqrt{\sigma_L^D}} = \frac{\sqrt{\sigma_S^P}\sqrt{\sigma_L^P}}{\sqrt{\sigma_L^D}} + \sqrt{\sigma_S^D}$$

Note that this equation has the form of y = mx+b, with:

$$y = \frac{\sigma_L\ (\cos\theta+1)}{2\sqrt{\sigma_L^D}}\ ;\ m = \sqrt{\sigma_S^P}\ ;\ x = \frac{\sqrt{\sigma_L^P}}{\sqrt{\sigma_L^D}}\ ;\ b = \sqrt{\sigma_S^D}$$

As such, the polar and dispersive components of the solid's surface energy are determined by the slope and intercept of the resulting graph. Of course, the problem at this point is that in order to make that graph, knowing the surface energy of the probe liquid is not enough, as it is necessary to know specifically how it breaks down into its polar and dispersive components as well. To do this, one can simply reverse the procedure by testing the probe liquid against a standard reference solid that is not capable of polar interactions, such as PTFE. If the contact angle of a sessile drop of the probe liquid

is measured on a PTFE surface with:

$$\sigma_S^P = 0$$

$$\sigma_S^D = 18.0\ \text{mN/m}$$

the principle equation reduces to:

$$\sigma_L^D = \frac{(\sigma_L\ (\cos\theta+1))^2}{72}$$

Since the total surface tension of the liquid is already known, this equation determines the dispersive component, and the difference between the total and dispersive components gives the polar component.

Accuracy/Precision

The accuracy and precision of this method is supported largely by the confidence level of the results for appropriate liquid/solid combinations (as seen, for example, in fig. 56). The Owens/Wendt theory is typically applicable to surfaces with low charge and moderate polarity. Some good examples are polymers that contain heteroatoms, such as PVC, polyurethanes, polyamides, polyesters, polyacrylates, and polycarbonates

The Fowkes Theory

The Fowkes theory (after F. M. Fowkes) is derived in a slightly different way from the Owens/Wendt theory, although the Fowkes theory's principle equation is mathematically equivalent to that of Owens and Wendt:

$$\frac{\sigma_L\ (\cos\theta+1)}{2} = \sqrt{\sigma_S^P}\sqrt{\sigma_L^P} + \sqrt{\sigma_S^D}\sqrt{\sigma_L^D}$$

Note that by dividing both sides of the equation by $\sqrt{\sigma_L^D}$, the Owens/Wendt principle equation is recovered. As such, one of the options for the proper determination of the surface energy components is the same. In addition to that method, it is also possible to simply do tests using liquids with no polar component to their surface energies, and then liquids that do have both polar and dispersive components, and then linearize the equations (see table). First, one performs the standard sessile drop contact angle measurement for the solid in

question and a liquid with a polar components of zero ($\sigma_L^P=0$; $\sigma_L = \sigma_L^D$) The second step is to use a second probe liquid that has both a dispersive and a polar component to its surface energy, and then solve for the unknowns algebraically. The Fowkes theory generally requires the use of only two probe liquids, as described above, and the recommended ones are diiodomethane, which should have no polar component due to its molecular symmetry, and water, which is commonly known to be a very polar liquid.

Accuracy/Precision

Though the principle equation is essentially identical to that of Owens and Wendt, the Fowkes theory in a larger sense has slightly different applications. Because it is derived from different principles than Owens/Wendt, the rest of the information that Fowkes theory is concerned with is related to adhesion. As such, it is more applicable to situations where adhesion occurs, and in general works better than does the Owens/Wendt theory when dealing with higher surface energies. In addition, there is an extended Fowkes theory, rooted in the same principles, but dividing the total surface energy into a sum of three rather than two components: surface energy due to dispersive interactions, polar interactions, and hydrogen bonding.[4]

The Wu Theory

The Wu theory (after Guo Xiong Wu) is also essentially similar to the Owens/Wendt and Fowkes theories, in that it divides surface energy into a polar and a dispersive component. The primary difference is that Wu uses the harmonic means rather than the geometric means of the known surface tensions, and subsequently the use of more rigorous mathematics is employed.

Accuracy/Precision

The Wu theory provides more accurate results than do the other two component theories, particularly for high surface energies. It does, however, suffer from one complication: because of the mathematics involved, the Wu theory yields two results for each component, one being the true result, and one being simply a consequence of the mathematics. The challenge at this point lies in interpreting which is the true result. Sometimes this is as simple as eliminating the result that makes no physical sense (a negative surface energy) or the result that is clearly incorrect by virtue of being many orders of magnitude larger or smaller than it should be. Sometimes interpretation is more tricky.

The Schultz Theory

The Schultz theory (after D. L. Schultz) is applicable only for very high energy solids. Again, it is similar to the theories of Owens, Wendt, Fowkes, and Wu, but is designed for a situation where conventional measurement required for those theories is impossible. In the class of solids with sufficiently high surface energy, most liquids wet the surface completely with a contact angle of zero degrees, and thus no useful data can be gathered. The Schultz theory and procedure calls to deposit a sessile drop of probe liquid on the solid surface in question, but this is all done while the system is submerged in yet another liquid, rather than being done in the open air. As a result, the higher "atmospheric" pressure due to the surrounding liquid causes the probe liquid droplet to compress so that there is a measurable contact angle.

Accuracy/Precision

This method is designed to be robust where the other methods don't even provide any results in particular. As such, it is indispensable, since it is the only way to use the sessile drop technique on very high surface energy solids. Its major drawback is the fact that it is far more complex, both in its mathematics and experimentally. The Schultz theory requires one to account for many more factors, as there is now the unusual interaction of the probe liquid phase with the surrounding liquid phase. In addition, the set up of the camera and backlight become more complicated owing to the refractive properties of the surrounding liquid, not to mention the set up of the two-liquid system itself.

Three component theories

The van Oss Theory

The van Oss theory separates the surface energy of solids and liquids into three components. It includes the dispersive surface energy, as before, and subdivides the polar component as being the sum of two more specific components: the surface energy due to acidic interactions (σ^+) and due to basic interactions (σ^-). The acid component theoretically describes a surface's propensity to have

polar interactions with a second surface that has the ability to act basic by donating electrons. Conversely, the base component of the surface energy describes the propensity of a surface to have polar interactions with another surface that acts acidic by accepting electrons. The principle equation for this theory is:

$$\sigma_L(\cos\theta + 1) = 2[\sqrt{\sigma_L^D\sigma_S^D} + \sqrt{\sigma_L^-\sigma_S^+} + \sqrt{\sigma_L^+\sigma_S^-}]$$

Again, the best way to deal with this theory, much like the two component theories, is to use at least three liquids (more can be used to get more results for statistical purposes) – one with only a dispersive component to its surface energy ($\sigma_L = \sigma_L^D$), one with only a dispersive and an acidic or basic component ($\sigma_L = \sigma_L^D + \sigma_L^+$), and finally either a liquid with a dispersive and a basic or acidic component (whichever the second probe liquid did not have ($\sigma_L = \sigma_L^D + \sigma_D^+$), or a liquid with all three components ($\sigma_L = \sigma_L^D + \sigma_D^+ + \sigma_L^-$) – and linearizing the results.

Accuracy/Precision

Being a three component theory, it is naturally more robust than other theories, particularly in cases where there is a great imbalance between the acid and base components of the polar surface energy. The van Oss theory is most suitable for testing the surface energies of inorganics, organometallics, and surface containing ions.The most significant difficulty of applying the van Oss theory is the fact that there is not much of an agreement in regards to a set of reference solids that can be used to characterize the acid and base components of potential probe liquids. There are however some liquids that are generally agreed to have known dispersive/acid/base components to their surface energies. Two of them are listed in table 1.

Table 1: List of common probe liquids

Liquid	Total Surface Tension (mN/m)	Dispersive Component (mN/m)	Polar Component (mN/m)	Acid Component (mN/m)	Base Component (mN/m)
Diiodomethane	50.8	50.8	0	0	0
Water	72.8	26.4	46.4	23.2	23.2

Potential Problems

The presence of surface active elements such as oxygen and sulfur will have a large impact on the measurements obtained with this technique. Surface active elements will exist in larger concentrations at the surface than in the bulk of the liquid, meaning that the total levels of these elements must be carefully controlled to a very low level. For example, the presence of only 50 ppm sulphur in liquid iron will reduce the surface tension by approximately 20%.

Practical Applications

The sessile drop technique has various applications for both materials engineering and straight characterization. In general, it is useful in determining the surface tension of liquids through the use of reference solids. There are various other specific applications which can be subdivided according to which of the above theories is most likely to be applicable to the circumstances:

The Zisman theory is mostly used for low energy surfaces and characterizes only the total surface energy. As such, it is probably most useful in cases that recall the conventional definition of surfaces, for example if a chemical engineer wants to know what the energy associated with fabricating a surface is. It may also be useful in cases where the surface energy has some effect on a spectroscopic technique being used on the solid in question. The two component theories would most likely be applicable to materials engineering questions about the practical interactions of liquids and solids. The Fowkes theory, since it is more suited for higher energy solid surfaces, and since much of it is rooted in theories about adhesion, would likely be suited for the characterization of interactions where the solids and liquids have a high affinity for one another, such as, logically enough, adhesives and adhesive coatings. The Owens/Wendt theory, which deals in low energy solid surfaces, would be helpful in characterizing the interactions where the solids and liquids do not have a strong affinity for one another – for example, the effectiveness of waterproofing. Polyurethanes and PVC are good examples of waterproof plastics. The Schultz theory is best used for the characterization of very high energy surfaces for which the other theories are ineffective, the most significant example being bare metals. The van Oss theory is most suitable for cases in which acid/base interaction is an important consideration. Examples include pigments, pharmaceuticals, and paper. Specifically, notable examples include both paper used for the regular purpose of printing, and the more specialized case of litmus paper, which in itself is used to characterize acidity and basicity

The Application of Methods of Measuring Surface Tension

The Capillary Rise Method: This methodology employs a small bore capillary which is inserted into the liquid whose surface tension is to be determined. The height to which the liquid rises in the tube is proportional to the surface tension.

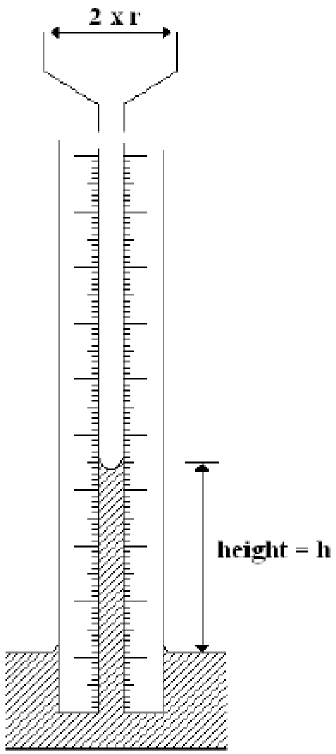


Fig. 56: Showing the diagram of the experimental Procedure of the Surface Tension by capillary rise method

To relate the surface tension to the height h we first consider a soap bubble whose radius r is the same as that of the capillary's bore. For the bubble, we have an Area (A) and a Volume (V):

$A = 4 \pi r^2$

$A = 4/3 \pi r^3$

If the pressure in the bubble is increased slightly, by P, the PV expansion work and the work required to increase the bubble's surface area will be, respectively:

$\delta W_{PV} = 4 \pi r^2 dr \Delta P$

$\delta W_A = \gamma 8 \pi r dr$

The expansion work is taken as just sufficient to expand the bubble's surface area, so we have:

$4 \pi r^2 dr \Delta P = \gamma 8 \pi r dr$

which gives us the so-called Laplace Equation:

$$\Delta P = \frac{2\gamma}{r}$$

Returning to our capillary rise experiment, the pressure difference on the hemispherical meniscus is equivalent to the

hydrostatic pressure of the liquid:

$\Delta P = dgh$

where d is the density of the fluid and g is the acceleration due to gravity. Combining this result with (Eq. 19) gives us:

$$dgh = \frac{2\gamma}{r}$$

$$\gamma = \frac{dghr}{2}$$ gives us our final result:

Experimentally, the radius of the capillary's bore is determined by calibrating the capillary using a fluid such as Water whose surface tension is known. Once calibrated, a simple height measurement will give us the surface tension. This derivation requires the meniscus be hemispherical. This can be achieved if the glass surface is thoroughly clean. Otherwise this will not be true and (Eq. 22) will not hold exactly.

Experimental Procdure

1. Prepare solutions of solutes to be measured. These will include:
   - 0.8M aqueous n-Butanol and 7 dilutions of this solution; each a ¾-fold dilution of the previous mix. n-Butanol is an irritant. Work with it in the Fume Hood.
   - Aq. Ethanol solutions at 20, 40, 60, 80, 100 wt%
2. Be sure the capillary is soaking in Chromic Acid cleaning solution. (The capillary should be stored in Distilled Water when not is use.)

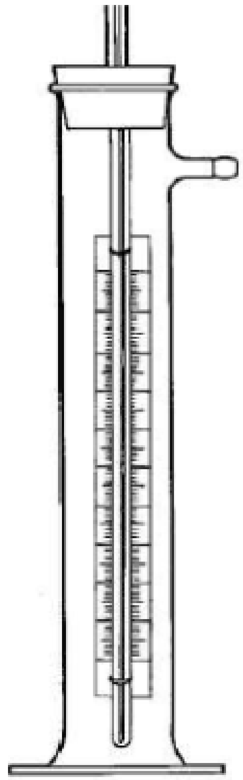


Fig. 57: The Surface Tension Apparatus

Pre-Lab Work

Work out a scheme for preparing about 100 mL of each of the above solutions.

1. Rinse the capillary thoroughly with

Instrumental Chemistry

Distilled Water. Also, rinse with the sample to be measured.

2. Calibrate each capillary you will be using against Distilled Water in the 25°C Water bath. The surface tension of Water over a range of 20°C to 40°C is given by:

$$\gamma\,[\text{dyne/cm}] = -0.15996\, t\,[^{\circ}\text{C}] + 75.96$$

with an error of 0.03%. Take at least five readings. Allow the meniscus to approach its equilibrium position from above and below. Be sure to read the position of the outside Water level.

Place about 100 mL of Distilled Water in the Surface Tension apparatus. Be sure the capillary, with its measuring ruler, is snuggly fit into the stopper and insert the stopper into the apparatus. Place the entire apparatus into the 25°C water bath. Allow it to stand for at least 10 minutes before taking any measurements. Be sure to read the correct temperature of the water bath with an immersion thermometer.

3. Measure the surface tension of Methanol over a range of temperatures from about 0°C to about 50°C. Each measurement should be made five times. Allow the

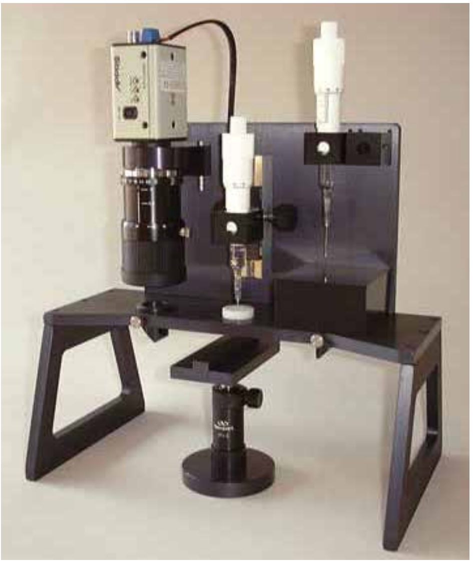


Fig. 58: A typical Advance Goniometer

meniscus to approach its equilibrium position from above and below, alternatively.

4. Measure the surface tension of the n-Butanol solutions. Each measurement should be made five times. Allow the meniscus to approach its equilibrium position from above and below, alternatively

Use of a Goniometer

A *goniometer* is an instrument that either measures an angle or allows an object to be rotated to a precise angular position. The term goniometry is derived from two Greek words, gōnia, meaning angle, and metron, meaning measure.

It is used for measuring the contact angle in the surface tension

Bellow we will see the use of a modern Goniometer.

Overview

The Firsttenangstroms (FTA32) goniometer provides video-based contact angle and surface tension measurements. Contact angles are measured by fitting a mathematical expression to the shape of the liquid drop and then calculating the slope of the tangent to the liquid drop at the liquid-solid-vapor (LSV) interface line. Computer software liquid drop shape analysis gives the contact angle without operator intervention or judgment.

Applications

Contact angle and surface tension for adhesion, cleanliness, wetting, biocompatibility.

Special Notes or Restrictions

Must be trained and qualified to use the tool.

Safety Precautions

Never touch the lens on the camera

Handle samples on the stage with gloves and/or tweezers.

Operation

Remove the cover on the lens.

Turn “ON” the computer if it is “OFF”.

Double click the “FTA32” icon on the desktop to start the operation.

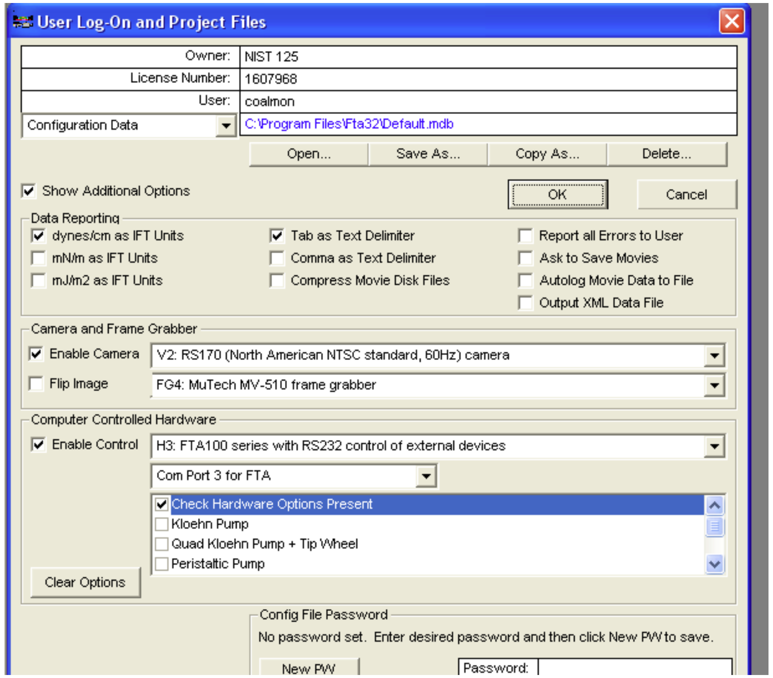


Fig. 59: Showing the Operation Window of the Software

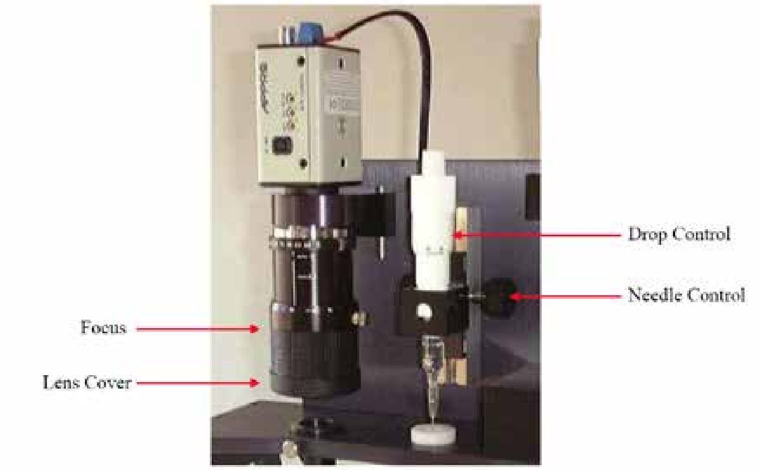


Fig. 60: The Different Parts of the Advanced Goniometer

Click "OK" to enter the program

Choose test fluid and place in syringe. Water is used in most cases because it is safe and forms a high, easily observed, contact angle on most materials. For other liquids, please consult contact engineer for feasibility.

Lock the syringe in the house tightly.

Click "Video" to show the image (see below).

Lower the needle to the view window and adjust the focus

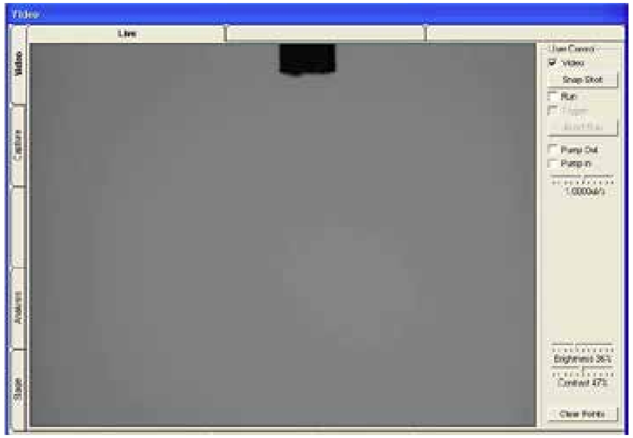


Fig. 61: Showing the Operation widow of the Advance goniometer software to see the liquid drop

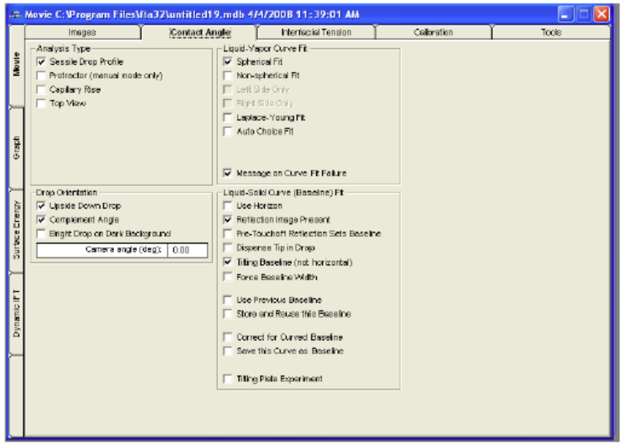


Fig. 62: Showing the Operation widow of the Advance goniometer software to see the liquid drop

until clear.

Load the sample on the holder and adjust the stage height to bring it into the view window.

Adjust the light and focus on the drop until clear and then click the "Snap Shot"

Define the contact angle analysis based on your need in the above window

Click "Contact Angle" to calculate the data (see below)

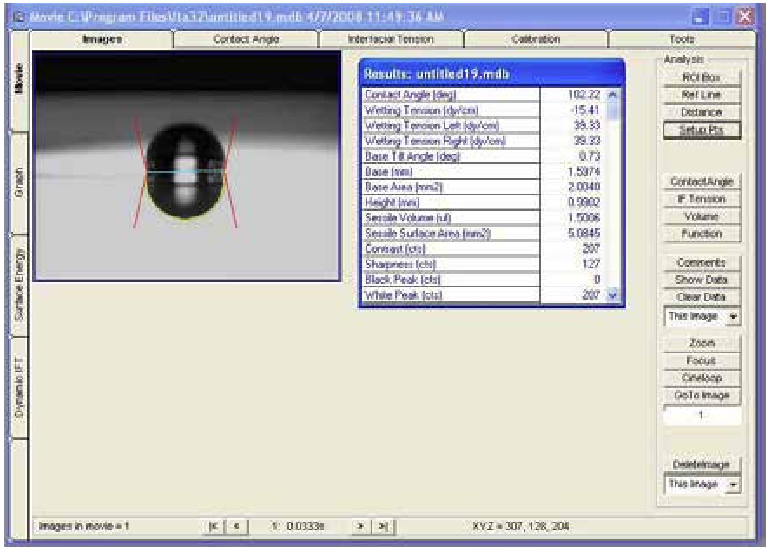


Fig. 63: Showing the Operation widow of the Advance goniometer software to see the liquid drop

Export the image from file menu and save it to the user folder.

End Steps

Raise the syringe back to the normal position.

Remove any liquid other than water from syringe.

Close the software.

Cover the camera lens.

Leave the computer ON